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Uses of Metals and Metallic Minerals



K.K. Chatterjee



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K.K. Chatterjee

Retd. Chief Mineral Economist,
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ISBN (13) : 978-81-224-2511-6

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NEW AGE INTERNATIONAL (P) LIMITED, PUBLISHERS

4835/24, Ansari Road, Daryaganj, New Delhi - 110002

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*“Education should be like the kindling of a flame
rather than like the filling of an empty vessel”*

— **Socrates**

Dedicated to my inner God.

PREFACE

Ideas keep flying all the time all over the universe, and I let my mind wander aimlessly into the realms of infinity; sometime some idea gets trapped inside my mind. That is how I got the idea of a book dealing with the uses of metals and minerals, some thirty years ago, when I was a junior officer in the Mineral Economics Division of Indian Bureau of Mines. Before that, for about fifteen years, I had been groping to know about why a product should require one particular grade of a particular mineral, and not some other grade or some other mineral. I never consider that use of a mineral or a metal is an independent entity; and to understand it fully, it should be linked backward with the history of evolution of the use and with the physical and chemical characteristics of the metal or the mineral; and it should be linked forward with the utilization of the wastes generated during and due to its processing or use, and with the prospects of its being substituted by some other material.

That is what I had been groping about, and that is how I decided to treat the subject thirty years ago. I got going in that direction making full use of the opportunities I got during my official tenure, for studying the workings of different industries and interacting with them; for rummaging through whatever relevant literature including physics, chemistry and metallurgy that I came across; and for surfing through internet and old United Nations and other study reports. For keeping myself up to date with news of new developments, the newsletters published by the Federation of Indian Mineral Industry, the Mining Metallurgical Geological Institute of India, and the Mining Engineers' Association of India, the journals and the newspapers were also helpful.

The book covering uses of the energy minerals has already been published in early 2006. Ever since then I have been receiving requests to write a book covering the other minerals. Presently I have chosen this group consisting of the metals (including the metalloids) and the metallic minerals in view of their historical significance to our civilization, and their importance to our present day economy.

While writing this book during the last several years, I have received physical and chemical support from many. I gratefully and most humbly remember them.

March 2007, Nagpur

Kaulir Kisor Chatterjee

INTRODUCTION

On an auspicious day, sometime around a million years ago, a member of the *Homo habilis* species stood erect and walked steadily on his two feet and his two hands became totally free. A new species – *Homo erectus*—began its journey on a new evolutionary track. This great change took around four million years after his ancestors – the hominids — broke free from the lineage of apes and chimpanzees. But , perhaps for the next seven to eight hundred thousand years, the descendants of that first *Homo erectus* kept wondering about what to do with the two free hands apart from holding bones and logs of wood.

That was till someone picked up a stone and threw it to some animal – probably because he was scared and was trying to defend himself, or because he was hungry and wanted to get some flesh to eat. But unconsciously, he began the gainful use of a mineral, and unconsciously again, began the evolution of a new species – *Homo sapiens*, the modern man. That first success with the stone thrown with the help of his hand triggered an altogether new evolution i.e., technological evolution. And a new age i.e., the Stone Age. Evolving down the generations, man learnt to be choosy in picking up the stones; he realized that all stones are not good for his needs; he tried and erred, and through innumerable trials and errors spanning over tens and hundreds of thousands of years, finally he zeroed in on a sharp-edged hard mineral that we have named flint. With the sharp edges of flint, he could tear animals for hide and flesh; and much later, he could make knives and axes and spear heads. Flint became the backbone of economy. Sometime along the evolutionary journey, on another auspicious day, he accidentally rubbed two pieces of flint and produced a spark of fire. That spark sparked off a revolution, a revolution within his head – a technological revolution. He has invented fire.

All along, he was dependent on only his muscle power for all his works. Now he has got a new power. With that trio of means at his command – muscle power, fire and flint – he began roasting the flesh for eating, and more. He began digging the earth, taking out new treasures and burning them. Thus was produced, some 6000 years ago, a new mineral, and from that a new material to which, much later, we have given the name copper metal. That day ended the Stone Age; that day probably marked the completion of his physiological evolution; and that day began the Copper Age. In fact, this was the beginning of both mining and metallurgy. With copper he could make better knives, better axes and better spears, and many new tools and objects of use. But not satisfied with copper any longer than a few hundred years, he began experiments with other metallic ores like tin, zinc and lead, and with a stroke of metallurgical genius, produced bronze. Much water flew under many bridges during the next two thousand years. By now, he knew about gold and silver also — not so much for industrial usage, but more for ornaments and amulets. Then came that wonder metal called iron. Man entered not only the Iron Age, but also what is known as the New World. Iron continues to be the backbone of economy even today, supported not just by copper, tin zinc, lead., gold and silver, but by a host of other metals.

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Although flint has survived the ages and still lives today — in name at least — in some cigarette lighters, we no longer use it for getting energy. Coal, petroleum, natural gas and uranium are the sources of energy now. But compared to the thousands of years of history of copper, lead, zinc tin, gold, silver and iron, the oldest amongst these energy minerals i.e., coal, has come to our life in a big way, only within the past 400 years or so. And we must not forget that for mining and using these energy minerals — and, in fact, all the minerals that we use today — we need machines, we need metals, we need metallic minerals — in America, in Europe, in China, in India. Even if we do not mine the metals, they still enter from soil into plants, and through plants into the cells, tissues and organs of human bodies, to help the humans live healthily. Such is the importance of metals and metallic minerals in industry, in economy and in human life.

From any mineral we do not get a metal. The minerals from which we get one, are called ores. Amongst the ores, there are many which are used only for extraction of metals, and there is no other use of them. There are also a few ores which have multiple uses. Of course the most important use is to extract their metal contents, but they can also be used straightaway for making industrial products. As a matter of convention, these are called metallic minerals in economic and statistical circles, to distinguish them from energy minerals and industrial minerals, which are not at all used for extraction of any metal. Examples of such metallic minerals are bauxite, hematite, chromite etc. The importance of these metallic minerals in Indian economy can be gauged from the fact that during the financial year ending March 2006, the total value of production of such minerals was 89.73 billion rupees i.e., about 12% of the total value of production of all minerals which was 751.22 billion rupees. And this despite the fact that the value of the metals has not been accounted for in these statistics. But again, the value of metals cannot just be measured in terms of rupees, we should also think what would have happened without the metals. There would not have been any industry, there would not have been any agriculture, there would not have been any civilization. Recognizing the need for projecting this importance of the metals and the metallic minerals, this book was conceptualized.

It is also recognized that without an idea of the history of evolution of the various uses of a metal, its present day uses will not be fully appreciated by the readers. It needs also to be recognized that those uses can only start with the recovery of the metal from its natural source mineral. Of course, as has been said, there are some direct industrial uses for metallic minerals in addition to their principal use i.e., recovery of metal values. So, all these aspects have been given due importance while laying emphasis on the uses of the metals.

Why is a particular metal or a metallic mineral used to perform a particular function or to make a particular product? That is because every metal possesses a unique combination of physical and chemical properties, and in this respect no two metals or two minerals are exactly the same. So a particular use of a metal or a mineral can be best understood if the use is linked to the particular set of physical and chemical criteria. And that has been done all through this book. Further, while dealing with physical and chemical criteria, invariably some technical terms pertaining to physics and chemistry are bound to come up. As far as possible, these terms have been explained in simple easily understandable manner in the glossary as well as in the text wherever they are encountered.

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Now, gone are the days when all the rich near-surface deposits of metallic minerals were there asking to be dug out and processed for extraction of their metal contents. Those deposits are all finished during the last thousands of years. Today, we are left with only the poor grade minerals from deep-seated deposits for our needs of metals. Can we use any grade of a mineral for recovering its metal value? The answer is yes and no.

The answer is yes, because firstly, man is not the producer of the mineral. The mineral was produced by nature hundreds of millions of years ago and stored in safe custody within rocks of the earth; what man does is only draw some quantity from nature's store house; and so, he has to accept whatever grade nature has created and whatever, out of the nature's treasure house, his forefathers have left for him. Secondly, recovery of metals from its minerals depend not on the grades alone, but on an interplay of four factors namely grade of the mineral, grades of other input materials for its processing, technology and prices of the final products based on the metal. Out of these, the price is determined by the market forces of demand-supply on which the producer has no control. But the other three factors are in the domain of the producer; he may mine a high grade mineral at a high cost, and use low grades of other input materials and employ low level technology to recover only a part of its rich metal value, or he may choose to mine an easily available low grade mineral at low cost, and use high grades of other input materials and employ high level technology to recover almost the whole of whatever metal values are contained in the mineral.

The answer is no, because at a given point of time there is a particular technology developed, and only one particular set of input materials with fixed qualities are available for processing a mineral. So, only one particular grade of the mineral can be processed with that technology and with those input materials, and only that particular grade has to be used at that point of time.

However, in today's fast developing situation, there is always a multiple choice available for technologies and grades of input materials. So, technology and input materials can be chosen to suit any grade of a metallic mineral that is available in nature. The only constraints are the market price and the cost of recovering the metal values. The cost has always to be less than the market price, the vagaries of which limit the range of flexibility regarding the specifications of grade. But, even if these specifications are not flexible enough at some point of time, the principles underlying the specifications remain valid all the time. And those principles, rather than the specifications, have been emphasized in this book.

The story does not, however, end with processing a mineral, recovering its metal values and using those metals for producing various consumer products. Nature has not given us minerals containing all metals, and nothing else. In exceptional cases, some pure gold nuggets were found, but they have all been taken away by our forefathers. As it stands today, though there are some metallic minerals like hematite with more than 65% of metal value, there are others that contain less than one percent. What happen to the huge quantities of material that are left out after the metal values are recovered? Such material may, in some cases, be even up to 99% or more of what is mined. Those are generally referred to as waste materials. Then there are wastages at the stage of manufacturing the consumer products out of the metals and the consumers themselves waste a lot of those products during and after their use. In fact, wastes generate at every stage of economic activity, but it has been the experience that yesterday's waste is today's asset and today's waste

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will be tomorrow's asset. This happens because the developments in technology are not only about recovering the metals, they are also about utilization of the so called wastes. After all, technology is for minimizing the costs at every level starting from mining of the mineral down to the final consumption, so that at every stage the cost is less than the market price.

The second consideration in favour of maximization of the utilization of the wastes is related to the environmental problems. Some of the wastes remain on the ground, some go to the rivers and the ground water, some go into the air. The pace at which mining and processing of metals are going on at present, is far faster than it was a few decades ago. Wastes are also being generated at a very fast pace. If nothing is utilized properly, then the amount of damage these wastes will cause to the land, water and air in a few decades hence, is unimaginable.

The third consideration is about concerns for conservation of mineral resources. Conservation as such is not a new concept. Emperor Ashoka thought about it about 2300 years ago. But he thought about conserving the forests, birds and animals. In the 3rd century BC, the edicts that he got inscribed on the rocks and iron pillars can be translated thus: " Twenty six years after my coronation, I declare that parrots, mynas, the aruna, ruddy geese, the nandimukha, cranes, bats, queen ants, terrapins, boneless fish, rhinoceros and all quadrupeds which are not edible are not to be killed; forests must not be burned". Conservation of mineral resources have become a concern only after the World War-II in 1945, when it was realized by the US Government, followed gradually by other governments, with alarm that higher grade parts of many minerals had all been mined out to meet the needs of the war and the economy, and there is urgent need to conserve what still remained. Conservation does not mean keeping the mineral deposits idle without mining. It means judicious mining, it means avoidance of wasteful practices of use, it means total utilization of the material mined without wastage. In other words, conservation means using not only the useful metal values of a mineral, but also the wastes generated during mining of the mineral to the maximum possible extent. Conservation and ignoring the waste materials generated during mining, processing or using of minerals and metals do not go together.

There is another dimension of the usage of metals and minerals – substitution. Though there are some metals which are indispensable in certain uses, there are also some which can be replaced by some other material in a use. This happens if the cost advantages of using a metal vis-à-vis its performance are lost and a cheaper and/or better material becomes available. A metal can be substituted either by another metal (e.g., copper by aluminium in electrical transmission wire) or by a nonmetallic substance (e.g., aluminium by plastics in construction material). In this book, issues related to both these dimensions – waste utilization and substitution, have been addressed with regard to their present and emerging trends, wherever relevant and important.

This book covers all these aspects for all the metallic minerals and metals that are economically important today. Besides, there are a few elements (six of them) which behave almost like metals, but still possess some characteristics like those of nonmetallic elements These are called metalloids (or semimetals). These are also of economic importance, and have been covered. It is hoped that this book should be of everyday use to not only the students and teachers of economic geology and metallurgy, but also to all those who are directly or indirectly concerned with metals and metallic minerals or are otherwise interested in knowing and understanding the whats, whys and hows of their uses.

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SECTION - 1

METALLIC MINERALS

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BAUXITE AND ALUMINIUM

Bauxite is primarily a metallic mineral though it is also used as an industrial mineral. It is the only ore used for large scale aluminium production. Although aluminium is the most abundant metallic element in the earth's crust constituting about 8%, it usually occurs in clays, soil and rocks that cannot be utilized for its extraction. Bauxite is actually not a distinct mineral species, but a generic term for a number of colloidal aluminium hydroxides like the trihydrate gibbsite ($\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}$), the alpha type monohydrate boehmite ($\text{Al}_2\text{O}_3, \text{H}_2\text{O}$) and the beta type monohydrate diasporite ($\text{Al}_2\text{O}_3, \text{H}_2\text{O}$). Although chemically, both boehmite and diasporite have the same composition, the former is a secondary mineral formed due to dehydration of gibbsite and is softer than the latter which is a product of metamorphism and is not suitable for metal recovery.

Commercially, the type of laterite (aluminous laterite) which contains sufficient quantities of gibbsite and boehmite, and is sufficiently rich in aluminium oxide (alumina) so as to enable its recovery, is referred to as bauxite. The chemical composition $\text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$ has been ascribed by Dana to this commercial bauxite, which, theoretically, contains 73.6% alumina, but in nature is associated with various impurities like iron oxide (hematite and magnetite), silica, clay and titanium oxide (rutile and anatase). In industry circle, aluminous laterite containing a minimum of 40% alumina is regarded as bauxite and that containing less than 40% alumina is regarded as ferruginous laterite. But geologically, there is no sharp dividing line, and there is always a transition zone containing marginally lower alumina which is sometimes called aluminous laterite and may be used for extraction of aluminium and for some industrial purposes.

Bauxite is a product of weathering (in contrast to diasporite which is a product of metamorphism). The name bauxite is derived from its first study area *Les Beaux* in south eastern France. It has been classified into laterite and terrarossa types. The laterite type bauxite is formed in situ from crystalline rocks and is rich in gibbsite. The terrarossa type bauxite overlies limestone or dolomite and is rich in boehmite.

HISTORY

The history of exploitation of bauxite can be traced back to 1821 when P. Berthier first analyzed samples collected from *Les Beaux* area in south eastern France. Later, around 1845-47, A. Dufrenoy named the mineral as "*beauxite*", which was changed to bauxite by H. Sainte-Claire Deville in 1861. Records of its first commercial mining is not available. Since aluminium was invented much later, probably bauxite was mined in the beginning for some nonmetallurgical uses.

However, an impetus to bauxite production seems to be synchronous with the beginning of aluminium industry. Although aluminium was first isolated in the laboratory in 1837, a commercial process of its recovery had to wait till 1886 when Charles Martin Hall in USA and Paul L. T. Heroult in France almost simultaneously (but independently) developed a technique for its extraction by electrolysis in fused cryolite. Development of dynamo to replace battery as a source of electricity triggered large scale production of aluminium. But its production did not pick up fast. By 1914, the world annual production was only 100000 tonnes and in 1918, it reached about 150000 tonnes. It was from the preparatory years before the World War-II (1940-1945) that the production really started picking up – mainly under the leadership of Germany – due to its demand in aircraft and other war-oriented industries. In 1937, the production reached the level of 500000 tonnes rising in 1941 to about one million tonnes and in 1943 to about 2 million tonnes. During the years immediately following the war, there was a declining trend in the production of aluminium metal; but potentialities for use of aluminium metal and alloys in everyday civil life started coming to light one by one after the war. In 1958 its production was 3.8 million tonnes; in 1963, 4.35 million tonnes; and in 1988, the production of aluminium was 13.37 million tonnes (pertaining to the erstwhile market economy countries that excluded the present Russia, China and other East European countries). By the year 2000, the world production of aluminium was 24.7 million tonnes. During the second half of the 20th century, the immense possibilities of its recycling also came to be recognized. According to the estimates of the US Bureau of Mines (1993), about 40% of the aluminium produced during 1988 was recycled to generate additional secondary metal.

So far as bauxite mining in the world is concerned, recorded data are available since 1934. During the 5-year period 1934-38, the total bauxite production in the world was about 14 million tonnes, i.e., an average annual production of about 2.8 million tonnes only. But due to stimulation of demand during the war, the total production during the next 5-year period (1939-43) jumped to over 35 million tonnes i.e., an average annual production of about 7 million tonnes. In 1948 it reached the level of 8 million tonnes and by the end of the century i.e., in 2000 it was 139 million tonnes.

In India, the history of bauxite can be traced to 1883, when F. R. Mallet of the Geological Survey of India (GSI) found some aluminium-rich laterite deposits in Jabalpur district in central India. These as well as many similar deposits in other parts of India like Bihar, Madhya Pradesh, Maharashtra and Tamil Nadu were of actually bauxite. Mining of bauxite commenced in 1908 in Katni area in Jabalpur district followed in 1920 in Khera district in Gujarat, and then the deposits of other areas were taken up from the 1940s onwards. But till 1944, in absence of an aluminium smelter in India, the bauxite was used for nonmetallurgical purposes.

The aluminium metal industry in India started only in 1943 when it was produced in Alwaye, Kerala for the first time by a company named Aluminium Production Company of India which was renamed in 1944 as Indian Aluminium Company Limited (INDAL). The production was initially based on imported alumina, but subsequently a plant for processing bauxite to alumina was set up in Muri in present Jharkhand. Another company by the name Aluminium Corporation of India started production in July, 1944 in its plant located in Jaykaynagar, West Bengal, and this plant is credited with producing the first aluminium ingot based on indigenous bauxite. INDAL set up its second smelter in 1959 in Hirakud, Orissa. In 1962, a third company named Hindustan Aluminium Company (HINDALCO) set up its smelter in Renukoot, Uttar Pradesh. In the same year, Madras Aluminium Company (MALCO) started production in its plant in Mettur dam, Tamil Nadu. Gradually other companies namely Bharat Aluminium Corporation (BALCO) and National Aluminium Corporation (NALCO) set up their plants in Korba, Chhattisgarh and Angul, Orissa respectively.

The production history of bauxite and aluminium in India is as follows.

<i>Year</i>	<i>Bauxite</i>	<i>Aluminium (Primary)</i>
1909 - 33	302000 tonnes	—
1934 - 43	114000 tonnes	1300 tonnes (only in 1943)
1944 - 46	40000 tonnes	11000 tonnes
1947	20000 tonnes	3000 tonnes
1950	65000 tonnes	4000 tonnes
1960	387000 tonnes	18000 tonnes
1970	1.37 million tonnes	161000 tonnes
1980	1.79 million tonnes	185000 tonnes
1990	4.85 million tonnes	433000 tonnes
April, 2000 to March 2001	7.99 million tonnes	624000 tonnes
April, 2002 to March, 2003	9.78 million tonnes	689000 tonnes

Most of the bauxite is used in metallurgical industry for production of primary aluminium metal. In addition, around 150000 tonnes of aluminium is recycled to produce secondary aluminium every year.

CRITERIA OF USE

The industrial usage of bauxite depends mainly on its chemical and mineralogical composition, and not so much on physical properties; but that of the products based on bauxite – mainly aluminium hydroxide, alumina and aluminium metal – depends more on physical properties. The principal ones amongst those criteria are as follows.

A. Bauxite

- (1) *Mineralogical composition:* Bauxite is made up mainly of a mixture of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Aluminium content of gibbsite is 65.35%, and that of boehmite is 84.98 per cent. A little amount of diasporite may also be present.
- (2) *Chemical composition:* Bauxite occurring in nature, contains 40-60% alumina (Al_2O_3), 15-30% H_2O , and the rest comprises iron oxides, SiO_2 and TiO_2 . The silica occurs in two forms – free silica and reactive silica. The former is that silica which occurs as such (e.g. quartz), and the latter is the silica occurring in combination with other minerals and chemicals as in clay. Free silica does not ordinarily take part in chemical reactions, but the reactive silica tends readily to react and combine to form new compounds depending on chemical affinity.
- (3) *Chemical resistance:* Bauxite is chemically resistant to sea water and ground water containing sulphate in solution.
- (4) *Chemical reaction:* Bauxite – more particularly gibbsite — dissolves easily in sulphuric acid hydrochloric acid and caustic soda.
- (5) *Softness:* Both gibbsite and boehmite are weathering products formed due to colloidal precipitation and are noncrystalline. Consequently, they are amenable to digestion in caustic soda at relatively low temperatures. Also, the water is not in any crystal lattice and

occupies only the pore spaces, rendering some softness to them. Between these two minerals, gibbsite containing thrice as much water is softer (hardness 2.5-3.5) and easier to digest, though it contains less aluminium.

- (6) *Effect of exposure:* Bauxite, when exposed to air, hardens rapidly.
- (7) *Effect of heat:* When heated to 400°C, gibbsite loses two of the three water molecules; when heated to 1650°C, bauxite becomes calcined; when heated to 2000°C, bauxite grains partially fuse to form sinter and crystalline alumina forms; and at still higher temperatures generated by electric arc, bauxite completely fuses, recrystallizes and becomes like natural corundum (aluminium oxide produced by metamorphosis and recrystallization).

B. Aluminium Hydroxide and Alumina

Aluminium hydroxide [$\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$], on heating gives off its water molecules and this decomposition is endothermic as the water absorbs heat. It is soft having hardness of 2.5-3.5 on Mohs scale, while the hardness of pure alumina is 9 (cf. natural corundum, the second hardest natural substance after diamond). Alumina fractures in subconchoidal to uneven pattern. Pure alumina melts at 3700°C; it is a good conductor of heat, and nonconductor of electricity. Both alumina and aluminium hydroxide are white coloured with high reflectivity.

C. Aluminium

- (1) *Colour:* Aluminium metal is silvery white. But coloured aluminium can be produced through anodizing (an electrolytic process for treating the surface); this produces a hard permeable oxide film, which readily absorbs coloured dyes.
- (2) *Lightness and strength:* Aluminium is one-third lighter than iron or brass. Its specific gravity is 2.7. Its strength to weight ratio is higher than steel.
- (3) *Ductility and tensile strength:* It is ductile—particularly when hot—enabling it to be drawn into wires and spun. However, when cold, its tensile strength is merely 25-50% that of copper, depending on the degree of annealing.
- (4) *Malleability and brittleness:* Aluminium is malleable when hot, but brittle when cold.
- (5) *Workability:* Due to the combination of the properties like ductility, strength, malleability etc., it can be fabricated easily into any shape—particularly in hot condition.
- (6) *Electrical conductivity:* Depending on purity, electric conductivity of aluminium varies from 62-64% and that of its alloys from 40 to 50% of the International Annealed Copper Standard or IACS (2.8 microhm/cm^3 at 20°C). If mass conductivity i.e., conductivity per unit mass, is considered, then for aluminium it is twice that of copper due to lower specific gravity of the former than the latter. Its electrical resistivity is 2.83 microhms-cm (cf. copper 1.7224).
- (7) *Thermal conductivity:* Thermal conductivity of pure aluminium is moderate when compared to copper (about 58% that of copper), but higher than many other metals. It varies from 0.52 to 0.56 calories/cm²/cm/ °C/second, while that in case of its alloys varies from 0.30 to 0.45 units.
- (8) *Melting and shrinkage:* Melting point of the metal is 660°C, and that of its alloys may be lower down to 450°C. Shrinkage of molten metal on solidification is gradual and low – only 6.6 per cent, and the melt flows easily without formation of shrinkage cavities.
- (9) *Wide range of liquid phase:* After melting at 660°C, aluminium does not boil till 2494°C.

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- (10) *Coefficient of expansion:* The coefficient of expansion of pure aluminium (23×10^{-6} per °C) is quite high – twice that of steel and 1.35 times that of copper. This facilitates extrudability of the metal in hot condition.
- (11) *Light and heat reflectance:* Aluminium metal sheets reflect 86% of radiated light and heat. This value in case of films made out of its sublimate is 90 per cent.
- (12) *Emissivity:* Emissivity is a measure of the energy (heat or some other form) appearing within a substance due to absorption of incident light. This is very low in case of aluminium – only 5 per cent.
- (13) *Affinity for oxygen and corrosion resistance:* Aluminium metal has a strong chemical affinity for oxygen. On exposure to air, a thin coating of aluminium oxide forms in a few seconds. This coating can protect the metal from further oxidation as well as from action of weak acids and salt water. The thickness and protective power of this coating can be increased by an electrolytic process in which aluminium is used as the anode immersed in a weak solution of sulphuric or chromic or boric or oxalic or phosphoric acid.
- (14) *Alloying ability:* Aluminium can alloy with a number of ferrous and nonferrous metals as well as a few nonmetals like silicon.
- (15) *Toxicity:* Aluminium is non-toxic.
- (16) *Inflammability:* Aluminium is not inflammable, but in presence of oxidizers, aluminium powder ignites at temperatures above 250°C.
- (17) *Recyclability:* Aluminium is recyclable practically endlessly.

USES OF BAUXITE

By far the most important use of bauxite is in metallurgical industry i.e., manufacturing of aluminium. But, it has a few nonmetallurgical uses also. In most of the uses, however, the products are based on an intermediate product namely, alumina which is made directly from bauxite. The important uses are:

1. Aluminium metal
2. Semi-fabricated products or semis
3. Semi-based products
4. Aluminium alloys
5. Die-casting (foundry)
6. Aluminium powder
7. Reinforced aluminium composites
8. Aluminium foam
9. Alon
10. Refractories
11. Abrasives
12. Chemicals
13. Aluminous cement
14. Desiccation
15. Petroleum refining and fertilizer manufacture
16. Catalyst and catalyst support

17. Pig iron and steel manufacturing
18. Plastics
19. Ceramics
20. Proppant in oil wells
21. Welding flux
22. Road aggregate
23. Paper
24. Rubber
25. Adhesives and sealants
26. Ball mill grinder
27. Artificial cordierite

These uses are discussed as follows:

1. Aluminium metal: The main deciding criteria are the chemical and mineralogical compositions, softness and solubility in caustic soda. Aluminium is produced in three stages – aluminium hydroxide [$\text{Al}(\text{OH})_3$], alumina (Al_2O_3) and aluminium. The most crucial is the first step i.e., production of aluminium hydroxide, and the process basically involves elimination of impurities like iron oxide, titanium dioxide, silica, silicates, phosphates, organics, vanadates, gallates etc. The most widely practised process for this is the Bayer process. In this process, bauxite is first crushed to (–) 100 mm size, ground along with waste caustic liquor recycled from the digestion unit, and then the slurry is retained for 8-10 hours at 95°C for desilicification. After this, the slurry is digested with caustic soda (NaOH) of concentration varying from 110 grammes/litre (g/l) to 170 g/l of Na_2O and at moderately high temperature varying from 100°C to 300°C . The optimum concentration of caustic soda and the optimum temperature depend mainly on the mineralogical composition of the bauxite and also on certain other parameters like energy consumption, extraction efficiency, capital and operating costs, etc. As a general rule, the concentration and temperature required are lower in case of gibbsite, and higher in case of boehmite. Similarly, while atmospheric pressure may serve the purpose in case of the former, higher pressure may be required in case of the latter. Digestion with low concentration caustic soda at low temperature resulting in production of coarse alumina is known as “American process” and that with high concentration caustic soda at high temperature resulting in production of fine alumina, as “European process” (the coarse alumina facilitates pollution control by scrubbing in the smelter). During digestion, bauxite reacts with NaOH to form a solution of sodium aluminate, while silica in the form a complex compound $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.\text{SiO}_2$ and the other impurities like iron oxide, titanium dioxide etc. remain insoluble. The solution is filtered out and the insoluble residue called *red mud* is disposed of. The solution is cooled to $50\text{-}80^\circ\text{C}$ and to it is added a few seed crystals of $\text{Al}(\text{OH})_3$, agitated and retained for 30-75 hours with a finishing temperature varying from $55\text{-}40^\circ\text{C}$ depending on the type of product desired. $\text{Al}(\text{OH})_3$ crystals precipitate from the solution and the sodium aluminate solution called *caustic liquor* is recycled for use and eventual recovery of part of the caustic soda (a part of the caustic soda gets lost in the $\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.\text{SiO}_2$). This $\text{Al}(\text{OH})_3$ product contains 10-12% moisture. In the second stage, the $\text{Al}(\text{OH})_3$ is calcined at $1000\text{-}1200^\circ\text{C}$ in rotary kiln or fluid bed calciner to obtain alumina (Al_2O_3), which may contain 0.4-0.6% soda, less than 0.1% iron oxide and silica, and traces of titanium dioxide.

The third stage is production of aluminium from the alumina. This is based on the classical Hall-Heroult technology. In this technology, alumina is dissolved in a fused electrolytic bath composed of aluminium fluoride (AlF_3) and cryolite ($3\text{NaF}\cdot\text{AlF}_3$). Now-a-days, after the only natural cryolite deposit in the world in Greenland has exhausted, synthetic cryolite is used. The cryolite bath dissolves about 10% of the alumina at the operating temperature of 920-970°C in the electrolytic cell. When high-intensity current is applied, the alumina dissociates into positive aluminium ions and negative oxygen ions, the former depositing on the cathode and the latter reacting with the carbon of the anode forming CO and/or CO_2 . The molten metal is tapped and cast into ingots. The used cryolite can be partially recycled. The technology is power-intensive. In Indian plants, power consumption generally varies between 16000 and 18000 kwh/tonne of metal with one exception i.e., NALCO plant in which the consumption norm is less than 14000 kwh. With improvement in cell design, the power consumption norm is coming down. The aluminium thus produced is of 99.8% purity i.e., commercial grade (CG) aluminium. For producing super-purity aluminium of 99.950–99.995% purity i.e., electrical conductor (EC) grade aluminium, the technology is somewhat different. In this technology, the bath in the electrolytic cell contains three layers – a bottom layer of aluminium-copper alloy; a middle layer of electrolyte comprising cryolite, barium fluoride and alumina; and the top layer in which the super-purity aluminium is deposited. To make still higher grade aluminium of 99.9990–99.9999% purity, a specialized technique known as “zone refining technique” is used. The properties of moderately low melting point, wide range of liquid phase and negligible shrinkage on solidification make it possible to produce aluminium economically.

2. Semi-fabricated products: The immediate downstream products of aluminium are the semi-fabricated ones, commonly referred to as “semis”. These are of two broad types:

- Flat products
- Non-flat products

Flat products include plates, strips, sheets etc., while the non-flat ones include tubes, pipes, rods, sections etc. These semis are made by two main processes namely, (i) casting followed by hot and cold rolling, and (ii) extrusion. There are different technologies for casting/rolling. The basic principle consists in first casting of molten metal into slabs (250–600 mm thickness) or thick strips or thin strips or rods or bars. While the slabs and strips are hot rolled into plates and coils which can then be cold rolled into thin gauge foils (0.005 mm thickness), the rods are drawn into wires and the bars are rolled into round billets for use as the input for extrusion. The principle of extrusion essentially consists of forcing a round billet heated in a closed container to 500°C to flow under an applied pressure (600 tonnes) through a die-opening and causing the metal to deform continuously into a long straight shape of predetermined dimensions. There is another technique called “impact extrusion” by which small thin discs are produced. In casting, as in the case of ingot metal, the main criteria are the relatively low melting point, wide liquid phase and negligible shrinkage on solidification, while for rolling and extrusion, the criteria are the malleability, easy expandability and extrudability of the metal when hot.

3. Semi-based consumer products: The properties of aluminium make the semis useful for shaping into different products of everyday use. There are over 3000 applications of aluminium known in the world, but in India, the number of applications is about 300. Broadly, its industrial use is limited to eight main sectors i.e., utensils, electrical, consumer durables, transportation, building and construction, canning and packaging, chemical processing, defence equipments, and one upcoming sector namely electronics.

- (i) *Utensils:* Easy workability, attractive colour, lightness, strong affinity for oxygen, and non-

toxicity make aluminium a cheaper substitute of copper in this use. While, the moderate thermal conductivity and moderately high melting point make it an inferior substitute for using it in cooking utensils, it is more suited for other kinds of utensils. The thin coating of oxide formed on its surface renders it corrosion-resistant. Commercial grade (CG) aluminium of 99.8% purity is enough for this application.

- (ii) *Electrical*: Electrical conductor (E.C.) grade aluminium of 99.950–99.995% purity is used in transmission lines as well as in appliances. Its high electrical conductivity, and ductility when hot make it a good and cheap substitute for copper in transmission lines. But, nevertheless, it is an inferior substitute, because of its lower conductivity for the same diameter. Besides, lower tensile strength makes it more susceptible to snapping, and lower-than-copper melting point makes it unsafe in case of short circuit. To compensate for the lower conductivity thick wires are used. Although this itself does not make the wire heavy due to its low specific gravity, its low tensile strength and consequent susceptibility to snapping requires the use of a core of steel wire around which the aluminium wire is stranded (aluminium conductor with steel-reinforced center), and this makes the cable heavy with a tendency to sag. But, primarily because of low cost and consequent security against theft, and less possibility of short circuits, aluminium wires are widely used in India for high and low tension overhead power transmission outdoor. Further, such overhead cables have no insulation cover, and any heat produced can escape; and even if there is lightning strike, mechanism is provided for protection against short circuit by making the lightning pass through the towers into the earth. Now-a-days, advanced metal matrix composite materials like ceramic fibre reinforced aluminium cable to carry high voltage without deformation, have been developed; but these are costly.

However, the situation regarding distribution of power within household and industrial premises is different. Here, a bunch of distribution lines are fixed along walls, roofs etc. and connected directly to lights, plugs, machines and switches. For safety, the wires are insulated and encased in casings. The thick steel-cored heavy wires make them unwieldy, and the large diameters of the wires make the cost of insulation high (which is not the case with copper wires whose diameters are small). Moreover, since the wires are connected directly to the devices and machines, they are liable to short circuits and sudden rise of temperature, causing them to melt unlike copper wires which have a considerably higher melting point. For indoor distribution lines, therefore, copper, and not aluminium, is preferred.

So far as electrical appliances are concerned, the high light reflectance combined with low emissivity and the high corrosion resistance of aluminium makes it suitable for use as light reflectors. The combination of lightness and electrical conductivity is the criterion in making condensers.

- (iii) *Consumer durables*: Here mainly sheets are used for making bodies of refrigerators and other household machines. Lightness, strength, colour, ability to take organic or inorganic colour coatings, corrosion resistance and workability are the chief criteria. Commercial grade (CG) aluminium is enough for this purpose.
- (iv) *Transportation*: Strength combined with light weight, natural and coated colours, corrosion resistance, and recyclability are the primary criteria for using aluminium in parts of the bodies of cars, trucks, vans etc., in wheel rims, in bumpers, in engine parts, in door panels of railway coaches and in aircrafts (also see under “Substitution” in the chapter “Iron Ore—Hematite”).

- (v) *Building and construction*: Strength combined with light weight, natural and coated colours, corrosion resistance and easy workability into any shape – strips, bars, angles, corrugated sheets, partition panels, perforated strips, door and window panels – make the commercial grade (CG) aluminium a good material in this sector. When used in roofing sheets, high heat reflectance and low emissivity add to its suitability.
- (vi) *Canning and packaging*: Thin discs produced by impact extrusion and thin-gauged plates and foils are used. The thin discs can be shaped into collapsible tubes such as those used for tooth-pastes and creams. From the thin plates are made boxes and containers. The foils are mostly used in cable wraps, cigarette foils, and for packing food and beverages. Easy workability, colour, lightness combined with strength and corrosion resistance are the main criteria. In addition, in case of food packs, the high thermal reflectance combined with low emissivity helps hot food to retain heat for long times. In sophisticated packaging, plastics laminated/coated with aluminium foil is used.
- (vii) *Chemical processing*: Storage tanks and pipes for chemicals, paints etc. use aluminium because mainly of its corrosion resistance which can be enhanced by increasing the thickness of the oxide coating, if necessary.
- (viii) *Defence equipments*: Primarily due to its lightness combined with strength, aluminium is used in mortar barrel mountings, missiles etc.
- (ix) *Electronic components*: Here, aluminium of very high purity containing 99.9990–99.9999% (five ‘9’ to six ‘9’ grade) is used for making capacitor foils and other components.

In many of the above applications, if cost escalation is permissible, some of the properties of aluminium are strengthened by alloying it with other metals or non-metals.

4. Aluminium alloys: Aluminium has good alloying abilities. The relatively more important of the standard alloys based on aluminium or containing significant percentages of it are listed below.

<i>Type of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(1) Ferro-aluminium	35-40% or 45-50% Al	De-oxidizer, de-sulphurizer and inclusion modifier for iron and steel industries; welding electrodes; hard-facing and de-oxidizing in powder form.
(2) Ferro-aluminium-calcium	25-30% Al; 15-30% Ca	De-oxidation and modification of inclusion for better mechanical properties and avoiding nozzle clogging during continuous casting.
(3) Ferro-titanium-aluminium powder	40% Ti; 10% Al	For welding electrodes, hard facing and de-oxidizing in powder form.
(4) Kanthal (iron-chromium-aluminium alloy)	75% Fe; 20% Cr; 4.5% Al; 0.5% Co	Can be used in oxidizing atmosphere at high temperatures up to 1350°C as in the case of making elements in high temperature furnaces.
(5) Duralumin	3 or 4% Cu with additions of Si, Mg and Mn	Aircraft frame.
(6) Wrought aluminium-magnesium alloy	2-7% Mg; up to 1% Mn	Medium strength and high corrosion resistance. Used in construction of marine auxiliary vessels.

<i>Type of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(7) Weldite	Al and Li	Strongest known wrought aluminium product, able to maintain superior strength over a wide range of temperatures; lighter than aluminium; weldable; can be used in oxidizer tanks in space vehicles and in aircrafts.
(8) Aluminium-magnesium-manganese	97.8% Al; 1.0% Mg and 1.2% Mn	Uses requiring high resistance to corrosion such as in roofing material.
(9) Aluminium-copper-magnesium-manganese	93.4% Al; 4.5% Cu; 1.5% Mg and 0.6% Mn	High strength with adequate workability; used in aircraft parts, truck wheels, etc.
(10) Aluminium-copper-silicon-magnesium	86.5% Al; 3.0% Cu; 9.5% Si; and 1.0% Mg	Casting alloys used in automotive pistons etc.
(11) Aluminium-zinc	Al, Zn and Mg	Combination of the properties of hardness and high strength midway between those of aluminium and ductile iron; cheaper alternative to bronze.
(12) Aluminium-cadmium-silicon	Cd in Al-Si matrix	Improved wear resistance and strength; used in highly loaded engine bearings.
(13) Aluminium-zinc-silicon-nickel-magnesium	Si, Ni, Mg added in a matrix of Al-Zn	Used in light alloy crankcases of vehicle engines.
(14) Low aluminium-tin	5.5-7.0% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium's machinability with improved strength; used in bearings where very high anti-friction properties are not essential.
(15) High aluminium-tin	20-40% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium's machinability with improved strength; used in bearings where very high anti-friction properties are essential.
(16) Aluminium-silicon	6.3-11.0% of fine Si particles evenly distributed in a matrix of Al with addition of 1.0-3.5% Cu.	High wear resistance, improved castability and corrosion resistance, decreased coefficient of expansion, elevated strength and ductility; used in pistons of automotive engines and bearings.
(17) Leaded aluminium alloys	8% Pb; 1% Cd; 1-4% Sn or Up to 10% Pb; 3-5% Cu; 0.5% Ni; 0.3-0.8% Mg or More than 10% Pb; small percentages of Cu, Mn, Zn, Fe and Si Or More than 17.5% Pb	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.

<i>Type of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(18) Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu; Al-Si alloys containing 2-24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base	Used in self-lubricating bearings and other antifriction applications.
(19) Aluminium-mica alloy	Mica coated with Ni or Cu with addition of Mg	Good solid lubricant; can be used in bearings.
(20) Aluminium-uranium alloy	U and Al	Possible use in nuclear reactors.
(21) Aluminium-zircon	Al and Zr	Medium strength.
(22) Silicon carbide fibre reinforced Titanium-aluminium alloy	Mainly Ti and Al	Combines ductility of aluminium with high temperature strength of titanium; suitable for use in spacecrafts.
(23) Wrought aluminium bronze	4-7% Al; may contain Ni, Fe, and Mn	Capable for deep drawing in cold operations, for resistance against corrosion and oxidation at high temperature; used imitation jewellery, cosmetic containers, pump rods, shafts, spindles etc.
(24) Aluminium-copper-lead alloy	93.5% Al; 5.5% Cu and 0.5% Pb	Suitable for extruded bar sections amenable to be cut freely.
(25) Aluminium-copper-bismuth alloy	93.5% Al; 5.5% Cu and 0.5% Bi	Used for mass produced components.
(26) Titanium-aluminium-vanadium alloy	Ti 90%; Al 6%; V 4%	Used in sheet and forgings for airframe parts, and in gas turbine compressor blades.
(27) Titanium aluminium tin alloy	Ti 91-94%; Al 4-6%; Sn 2-3%	Used in aircraft tailpipe assemblies, sheet components subjected to up to 500°C temperature, gas turbine compressor rings, missile fuel tanks.
(28) Titanium-aluminium-molybdenum-tin-silicon alloy	Ti 87.5%; Al, Mo and Sn each 4%; Si 0.5%	High strength alloy, used for highly stressed structural components in aircraft and structural engineering.
(29) Titanium-aluminium-molybdenum alpha-beta alloy	Ti 89%; Al 7%; Mo 4%.	Poor weldability, but high strength at high temperature; shallow hardening.
(30) Titanium-vanadium-chromium-aluminium beta alloy	Ti 73%; V 13%; Cr 11%; Al 3%	Better weldability than the alpha-beta alloy; high density; thermally stable above 370°C; amenability to cold working. Used in cold-headed bolts.

<i>Type of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(31) High-duty aluminium-bronze	Cu 79.5% ; Al 9.5%; Fe 4.5%; Ni 5.5%; Mn 1%	Superior corrosion resistance in marine conditions; also high wear resistance.
(32) High tensile brass	Cu 55%; Zn 38%; Al 2%; Fe 2%; Mn 3%	Used where high-strength castings are required, as in marine propellers.
(33) Die-casting brass	Cu 60%; Zn 39.5%; Al 0.5%	Used for general purpose die-casting works.
(34) Nimonic	Ni 58%; Cr 20%; Co 17%; Ti 2.5%; Al 1.5%; C 0.13%(max)	Creep resistant at temperatures up to 920°C. Used in gas turbine blades and discs, hot-working tools

The corrosion resistance of alloy sheets containing small amounts of manganese or magnesium can be further improved by giving the material a surface coating of pure aluminium, and this product is called “*alclad*”.

5. Die-casting (foundry): Aluminium is becoming a substitute of the more traditional metal zinc in this application. Meltability, wide liquid phase, lightness, attractive colour and ability to take dyes, low shrinkage and strength are the criteria. Molten aluminium can be die-cast into any odd shaped small components like car handles, carburetors, door handles etc.

6. Aluminium powder: Aluminium powders may be in the form superfine powders (5 microns) or granules or flakes (up to 8 mm), and can be made by (i) solid phase decomposition, thermal decomposition, liquid phase precipitation and gas phase precipitation, (ii) comminution (i.e., size reduction), machining, milling and impact attrition (grinding in ball mills in presence of edible vegetable oil or food grade fatty acids), and (iii) atomization by subjecting a molten stream of metal to air or inert gas or water jet under pressure to create a fine spray of very fine droplets, and then, if granules or flakes are to be produced, by subjecting the spray to centrifugal spinning from a disc or cup (for further details see the chapter “Iron Ore—Hematite”). Aluminium powder is used (i) in powder metallurgy (ii) in aluminium paint (iii) for aluminium coating of metal surfaces (iv) blasting agent, (v) rocket fuel, (vi) bio-degradable detergents, and (vii) fillers in epoxies.

Powder metallurgy is the process whereby many small components are produced by fabricating metal powders or metal and ceramic powders or alloying mix of metals together. It permits the production of a broad spectrum of complex alloys with high degrees of homogeneity and fine-scale microstructure. Fabrication techniques are as follows.

- (i) *Press and sinter:* This technique results in semi-dense parts and components. Compaction is performed in a die under high pressure (40-60 tonnes per square inch). A lubricant is mixed with the powder. The mixture is then sintered (i.e., heated to less than melting point) in order to bond the material.
- (ii) *Injection moulding:* This is employed to allow for moulding of metal and ceramic powders.
- (iii) *Hot consolidation:* By this technique, dense wrought alloys can be produced. The methods include hot isostatic pressing, powder forging, hot extrusion, dynamic compaction and powder rolling.

Aluminium powder metallurgy offers components with exceptional mechanical and fatigue properties, low density, corrosion resistance, high thermal and electrical conductivity, excellent machinability, good response to a variety of finishing processes. Magnetic alloys made by powder methods have uniform flux density and fine grain structure (e.g., Al-Ni-Fe and Al-Ni-Fe-Co alloys used in permanent magnets).

Aluminium paint is applied to machinery, containers, tanks, pipes, agricultural plants, important structures etc. to render to the painted surfaces resistance to heat (up to 250°C) and corrosion, tough extra-bright surface finish. Styrene-modified oil, alkyd resin, white spirit, solvent naphtha, butyl glycol etc. are generally used as bases for making a paste which can be applied by brush or roller or spray depending on the area to be painted.

Aluminium powder can also be applied directly as a metallic coating instead of in the form of a paint. The methods include spraying, aluminizing (i.e., heat-treated sprayed coatings), hot dipping, electroplating, gas/vapour plating, cladding (i.e., mechanical bonding). The thickness of coating varies from 0.025 to 2.5 mm.

In blasting and rocket fuel, the strong affinity of aluminium to oxygen and the tendency of its powder to ignite, when heated in presence of an oxidizing substance is taken advantage of. Aluminium burns with bright flashes and loud bangs in explosives and fire crackers. In rockets, it helps the solid propellant system (solid propellant consists of an oxidizer, a fuel and a binder—all in solid state) to provide the necessary thrust.

In biodegradable detergent, it is used for removing stubborn stains (chewing gum, adhesives, grease etc) from fabric, garage and workshop floors etc. by virtue of a mild abrasive action. It also gives a shining effect to bench tops, chrome/porcelain baths, sinks etc. and brighten grey, weathered timber. It serves as an optical brightener.

7. Reinforced aluminium composites: Advanced metal matrix composite (MMC) materials include aluminium reinforced by

- particulate SiC suitable billets for extrusion with very good dimensional stability,
- whiskers and fibres of SiC for use in advanced tactical fighters and rocket motor cases,
- boron fibre to produce aluminium sheets for conversion to tubing for use in space shuttle, and also to produce consumer products like bicycle frames, golf carts, boats, masts, propellers and skis,
- Al₂O₃ fibre to make aluminium engine connecting rods,
- Al₂O₃-SiO₂ fibres to make aluminium pistons which are less prone to cracking.

8. Aluminium foam: It is a light weight version of pure aluminium with honeycomb-like structure and has a five times lower density. It is as strong as pure aluminium, has high shock resistance, is not inflammable and is blast resistant. It can be used in building structures, railway wagons, car bodies etc. It has started replacing steel in construction and automobile industry.

9. ALON: This is the acronym for aluminium oxy-nitride. It is very light and an excellent electrical insulator. It has wide applications in aircraft and defence. It can also be made transparent like glass with excellent glossy and scratch-resistant surface. It is also used in a more advanced form of “*electrode boring*” called “*electrochemical boring*”. These are techniques of making very fine bores (diameter may be as small as 0.004 mm). In conventional electrode boring, a fine platinum wire electrode is inserted within a glass tube, and positive and negative electrical charges from a DC source are applied to the object to be bored and to the electrode tube respectively. Due to flow of electrons, molecules of the object are eroded at the point of its contact with the platinum wire. In electrochemical boring, an electrically conductive thin metal tube containing an electrolyte is used in place of the platinum-glass electrode. Here, role of ALON is to provide a very thin insulating coating on the metal tube with a view to preventing electrochemical corrosion of the object around the contact point.

10. Refractories: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580°C. The function of refractory lining is not only to withstand high temperature, but also to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slags and metals. Alumina is used for making some types of high-alumina refractories, and different alumina-bearing minerals like clay, bauxite, corundum, kyanite and sillimanite may be the raw material. The alumina-content in such refractories varies from 30-100 per cent. If the alumina-content is more than 45-50%, then bauxite is used as the starting point, and its chemical composition is the main criterion. Such refractories are used for lining rotary cement kilns and metal working furnaces where corrosion from basic materials is expected. They can be of the following types depending on the basic material, the process and the properties:

- (i) *Calcined bauxite:* The alumina is not the pure one produced by Bayer's process via aluminium hydroxide, and instead, is produced by calcination of bauxite at a temperature of 1650°C by which free and combined water is removed. Calcination is carried out in vertical kiln, and the charge comprises alternate layers of coke, grits and bauxite lumps. The clays contained in the bauxite become mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and the bauxite itself is transformed into what is called alpha-alumina (an aggregate of ultra-fine crystals). This highly dense product is then moulded into bricks which are fired to yield a dense dimensionally stable refractory product. Such refractory bricks have a fusion temperature varying from 1600-1900°C depending on the purity of the bauxite, and are particularly suitable for lining the roofs of electric arc steel furnaces, blast furnaces, ladles etc.
- (ii) *Sintered bauxite:* When the bauxite is low in clay content, there will be less mullite formation on calcination. Such bauxite is crushed to 12 micron size and heated to 2000°C. The particles are partially fused and they join together to yield a strong product known as sintered bauxite.
- (iii) *Calcined alumina:* This alumina is not produced directly from bauxite as in the cases of the above, but is the product of drying of $\text{Al}(\text{OH})_3$ produced by Bayer's process. The high-purity alumina is calcined, and the calcined alumina has a high melting point of 3700°C and also is very hard, its hardness being equal to that of natural corundum i.e., 9 on Mohs scale. Consequently, the refractory bricks made of it are suitable for use in areas where they are subjected to both high temperature and abrasion (e.g., injection gates and sliding gates in iron and steel plants). However, in this case, additional care has to be taken for removal of sodium, if any, from the $\text{Al}(\text{OH})_3$ by adding boric acid after digestion, because the sodium in the form of Na_2O is carried into the alumina, and when this alumina is calcined, it forms a low melting glass. This glass eventually decreases the refractoriness of the product.
- (iv) *Sintered alumina:* It is also called '*tabular alumina*' because the alumina crystals become hexagonal elongated table shaped. Sintering is done at 1925°C to obtain a highly dense product. Its refractoriness and abrasion resistance properties as well as applications are similar to calcined alumina. But this is used in the form of aggregates instead of bricks.
- (v) *Calcium aluminate cement or CAC:* This is the product of reaction of high purity alumina with limestone. This refractory cement is used for monolithic applications such as in blast furnace troughs, ladle lining etc. (see "cement" at serial number 13).
- (vi) *Alumina graphite refractories:* These contain 50% alumina and 30% graphite. These are highly resistant to wetting by molten steel and are used in continuing casting, torpedo ladles etc.

- (vii) *Alumina zirconia silica refractories*: They contain 50% alumina and up to 40% zirconia and silica. They may either be moulded into bricks for furnace lining or made into an aggregate for ramming of contact zones. Their most important application is in glass furnaces.
- (viii) *Chrome-alumina bricks*: This is one of the latest products which is gaining popularity. In this type of bricks, fine particles of chromite or pure Cr_2O_3 is incorporated in high alumina refractories to the extent of 3.5-5.0% as the binding matrix. The Cr_2O_3 forms solid solution in Al_2O_3 , forming a dense layer at the slag/refractory interface. This results in reduction in slag penetration and reaction at elevated temperature due to increased viscosity of the glassy phase of the refractory.

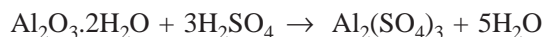
11. Abrasives: Abrasive property of a substance depends primarily on fracture pattern, toughness of grains, and hardness. The substance should break into grains with subconchoidal to uneven surface (conchoidal fracture may scratch and damage the surface being scraped) and it should be harder than the surface to be ground and polished. Also, the individual grains should be tough enough to withstand the stress and strain of grinding, and for this, there should not be micro-fractures within the grains. Bauxite-based abrasives may be of the following types:

- (i) *Brown fused alumina*: This is made by first calcining bauxite at 1100°C (cf. 1650°C in case of calcined bauxite refractory for mullite formation), and then fusing the calcined bauxite along with coke in electric arc furnace at $2100\text{-}2200^\circ\text{C}$. After fusion, the melt is slowly cooled which results in the crystallization of alumina. The coke serves to reduce iron oxide and silica to a iron-silicon slag. Iron pieces may be added to the melt, if the iron content is less than what is required for formation of slag. This slag is magnetically susceptible, and can be separated by magnetic separation methods. Even then, some residual iron oxide remains and this renders the mass of fused alumina brown. This brown coloured mass is crushed and ground. It is used in bonded and coated abrasives, such as grinding wheels, belts etc. It is a tough abrasive suitable for polishing high strength materials like bronze, steel and hard wood.
- (ii) *White fused alumina*: This is produced by fusing in an electric arc furnace at $2100\text{-}2200^\circ\text{C}$, pure alumina produced by Bayer's process via aluminium hydroxide. Chromium oxide may also be added to the furnace. The fused mass, after slowly cooling as in the case of brown fused alumina, is crushed to produce granular alumina which is less tough (i.e., more friable) but harder compared to brown fused alumina, and hence, it produces less friction heat. It is, therefore, more suitable for polishing optical glass, heat-sensitive metals etc.
- (iii) *Aluminium hydroxide*: Its hardness is 2.5-3.5 on Mohs scale, and can be used as an abrasive for soft applications, such as on plastics.
- (iv) *Calcined alumina*: As has been described in case of calcined alumina refractories, this material of high purity has hardness equal to that of corundum—9 on Mohs scale—when fully calcined, and is also called "*artificial corundum*". It can withstand intense heat, and breaks in subconchoidal to uneven fracture pattern. Its crystal shape and grain size – and hence hardness and toughness—can be controlled and manipulated by varying and controlling the conditions of crystallization and calcination of alumina. The crystal growth is manipulated in such a manner as to minimize development of fractures within the crystals, and hence, to enhance toughness. Also, grains of different hardness and toughness can be blended in different ratios to suit an application.

- (v) *Artificial emery*: Emery is a mixture of corundum with either magnetite or hematite in loose granular form (vide chapter “Iron Ore--Magnetite). Calcined bauxite grains can also be mixed with magnetite to produce artificial emery, and since the latter is softer than the former, their ratio can be varied to adjust the resultant hardness of the emery to suit an application.
- (vi) *Alumina zirconia abrasives*: If 25-40% of zircon sand and the balance pure Bayer’s alumina, are fused together and suddenly cooled, a solid solution of zirconia and alumina with growth of sharp dendritic microcrystalline structure in the grains, results. This abrasive can be used for sharpening purpose. Zirconia serves to increase the toughness, but not the hardness, of the abrasive.
- (vii) *Seeded alumina gel*: Alumina gel belongs to the general class of compounds “*alumoxanes*”. It can be prepared by dissolving solid colloids of aluminium hydroxide in some organic solvent and then precipitating the oxide, or by hydrolysis of aluminium alkoxides, or during polymerization of ethylene with aluminium alkyls. These gels are subjected to wet vibratory milling with alumina medium. During milling, the alumina of the medium as well as zinc and iron from the piping material gets introduced into the gel. These materials act as the seeds. The seeding can also be achieved by direct addition of about 1% of ultra-fine alpha alumina polycrystalline bodies of not more than 0.4 micron size. The seeded aluminium gels grow to about one micron size. The milled mix is poured into containers, dried and crushed to obtain polycrystalline grits which are sintered at 1100-1500°C to make abrasive grains. Alternately, the grits are moulded into shapes or extruded as rods and cut into pieces to make abrasives blocks or rods. This process enhances the hardness of the abrasives considerably.

12. Chemicals: Different aluminium chemicals are manufactured based on either bauxite or aluminium hydroxide or alumina. These are as follows.

- (i) *Aluminium sulphate* [$Al_2(SO_4)_3$]: This may be of two types—ferric and iron-free. The ferric grade $Al_2(SO_4)_3$ is variously termed as ferrous alumina, alumina (ferric), aluminoferric and ferric alum cake. It is prepared by digesting bauxite ground to 200 mesh size in sulphuric acid. The chemical reaction is:



The solution is evaporated to get solid $Al_2(SO_4)_3$ crystals that contain relatively low percentage of alumina varying from 14-18% depending on the latter’s content in the bauxite.

The iron-free $Al_2(SO_4)_3$ is based on very pure Bayer’s $Al(OH)_3$ instead of bauxite. The hydroxide is digested with sulphuric acid at 110°C for 20 hours. The resultant $Al_2(SO_4)_3$ contains 69-70% alumina and almost nil FeO (0.005-0.010%).

Iron-free $Al_2(SO_4)_3$ is used for purification of town and industrial water, for treatment of sewage water, for fixing size of resin in paper and tanning industries, for fixing colour of dyes of paper, leather etc., and as deodourant and de-colourant of mineral water. The ferric $Al_2(SO_4)_3$ is used in water purification mainly. When added to water, it releases positively charged hydroxide ions which coagulate the negatively charged impurities including pathogenic organisms. Other minor uses of $Al_2(SO_4)_3$ are in pharmacy, foam fire extinguishers, printing ink, fire resistant paints, water-proof textiles, cement, rubber fillers and plastics.

(ii) *Alums*: These are hydrated double sulphates of aluminium with potassium [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or potash alum] or with sodium [$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or soda alum] or with ammonium [$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or ammonia alum]. Until 1928, in India particularly, soda and potash alums used to be obtained from natural alum shale, which occurs as thin beds of shale with very small grains of pyrites disseminated in them. Different kinds of alums were prepared by exposing or firing this pyritiferous shale, followed by lixiviation with water, and then by treating the liquor with solutions of rehmitti (soda alum) or with saltpeter (potash alum). Alumina came from the shale. Apart from shale, other naturally occurring minerals namely apjohnite [$MgSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$], aluminite [$Al_2O_3 \cdot SO_3 \cdot 9H_2O$], halotrichite [$FeSO_4 \cdot Al_2(SO_4)_3 \cdot 2H_2O$], kalinite [$KAl(SO_4)_2 \cdot 12H_2O$], mendozite [$NaAl(SO_4)_2 \cdot 12H_2O$], pickeringite [$MgSO_4 \cdot Al_2(SO_4)_3 \cdot 22H_2O$], tschermigite [$(NH_4)Al(SO_4)_2 \cdot 12H_2O$] served as the source material.

After 1928, alums are prepared with bauxite as the starting material. But now-a-days, soda and potash alums have more or less been discarded and replaced by ammonium alum. The first step of the process involves digesting bauxite with H_2SO_4 much the same way as ferric grade $Al_2(SO_4)_3$. Thereafter, the liquor is mixed with ammonium solution, concentrated and dried.

The uses of alum are the same as those of $Al_2(SO_4)_3$.

- (iii) *Aluminium chloride*: This may be in either anhydrous ($AlCl_3$) or hydrate ($AlCl_3 \cdot 6H_2O$) form. It is prepared by dissolving calcined bauxite in HCl acid. Its uses include metal finishing, preservative, wool carbonizing, petroleum refining, bleaching, cosmetics, pharmaceuticals, production of titanium dioxide pigment, making of some organic compounds, and catalysis in the manufacture of certain drugs, dyes and perfumes. The hydrate is also suitable for water purification because of its ability to flocculate the impurities.
- (iv) *Aluminium fluoride*: Aluminium fluoride (AlF_3) is manufactured by treating alumina with hydrofluoric acid or fluorosilicic acid. Its main uses are in metallurgical industries as a flux for melting aluminium and for casting, soldering, welding etc. Its nonmetallurgical uses are in opacifiers for optical and special glasses, enamels and ceramic products, and in the manufacture of aluminium silicate fibres.
- (v) *Aluminium carboxylates*: The monostearate, distearate and tristearate of aluminium belong to the aluminium carboxylate family. They have a strong ability to gel vegetable oil and hydrocarbons, and for this reason are used as fixing agents in waterproofing and dyeing of textiles. They find wide application in the cosmetic industry for preparation of clear cosmetic gels and pomades. They are also antiseptic and astringent agents, are used in the preparation of analgesic and antipyretic drugs. New applications include lubricants for adding to drilling mud for increasing the bit bearing life. The manufacturing process starts with preparation of sodium stearate by reaction of soda ash with stearic acid. Then aluminium stearate is manufactured by double decomposition of sodium stearate with aluminium chloride.
- (vi) *Other organic compounds*: Aluminium chlorhydroxide and aluminium glycinate are used in some kinds of deodourant and antiperspirant.
- (vii) *Aluminium nitrate nonohydrate* [$Al(NO_3)_3 \cdot 9H_2O$]: This is prepared by digesting either alumina or aluminium hydroxide in dilute nitric acid and precipitating the aluminium nitrate as white crystals. If the alumina is re-extracted, it assumes insulating properties and

is used for making insulating papers for wrapping transformer core laminates and cathode ray tube heating elements. Its other main use is in extraction of actinides.

- (viii) *Sodium aluminate*[$Na_2Al_2O_4$]: In metallurgical industry, its formation is an intermediate stage in the Bayer's process of manufacturing aluminium hydroxide, when bauxite is digested in caustic soda. But there, due to presence of silica in the bauxite as an impurity, it reacts with that silica and forms sodium aluminosilicate. But when it is manufactured exclusively as a chemical, relatively pure silica-free bauxite is digested with caustic soda. It has some unique properties such as easy reactivity with silica to form and precipitate sodium aluminosilicate, aiding precipitation of soluble phosphate, aiding the coagulating ability of other chemicals making it useful in treatment of municipal drinking water, sewage water and boiler water, and also for softening of hard water. Also it is used for fixing resin and dyes in paper manufacturing, for preventing chalking of outdoor paints, and in manufacture of glass, ceramics and acrylic fibre.
- (ix) *Aluminium hydroxide gel*: Aluminium hydroxide gel is a suspension containing the equivalent of not less than 3.6% and not more than 4.4% Al_2O_3 . The aluminium hydroxide gel, when dried, is a white, odourless, colourless and tasteless substance. This gel is not the seeded one used as abrasive. It is used as an antacid and protective in the treatment of peptic ulcers; it is also an astringent and antiseptic used for treating hyperacidity. For manufacturing this chemical grade gel, the starting material is aluminium sulphate which is dissolved in distilled water. Then sodium carbonate is added slowly to convert the sulphate solution to aluminium hydroxide, which is then filtered, washed in distilled water, dried at 65-70°C, pulverized and packed.

13. Cement: Cement from the point of view of use of bauxite in the raw material mix, may be (a) aluminous or high-alumina cement, and (b) Ordinary Portland cement. The main difference between these two types of cement is that the principal constituent of high-alumina cement is mono-calcium aluminate and that of the Portland cement is tri-calcium silicate. Consequently, while the Al_2O_3 content in the former is very high (of the order of 50-60% compared to around 5-10% in the latter), CaO and SiO_2 contents in the latter is high (of the order of 60-70% and 20-25% respectively compared to around 30-40% and 5-10% respectively in the latter). On mixing with water, the mono-calcium aluminate of high-alumina cement transforms into di-calcium aluminate with liberation of gelatinous alumina, whereas the tri-calcium silicate of Ordinary Portland cement becomes mono-calcium silicate and lime.

(a) *High-alumina cement*: Its properties include quick setting (2-4 hours), high strength achieved in 24 hours, and ability to withstand high temperatures up to 1200°C. There are two types of high-alumina cement namely, (i) High iron (also called *ciment fondu*) and (ii) low iron. Both these types are used, along with a suitable aggregate of refractory grog, as refractory cement or refractory mortar for applying on refractory linings, and also as castable refractories.

After setting, the high iron type rapidly becomes hard and resistant to corrosion by chemical attack. It is manufactured by melting a mixture of lumpy high-iron bauxite, limestone and coke in a vertical shaft furnace in which the rising volatile gases preheat the feed before its melting. The melt is then cast into ingots, solidified and ground. The iron contributes to hardening properties. Its rapid-hardening properties, resistance to sea water and ground water containing sulphates in solution, and impermeability make it suitable for use in the construction of reservoirs and foundations in marshy conditions, of piers and harbour works, of drainage and sewerage pipes, of internal linings of water tunnels, of power station flue gas chimneys etc.

For manufacturing the low-iron type, chalk or limestone fines and low-iron bauxite fines are mixed and melted in an electric arc furnace. It is more refractory than the high-iron type, but not as hard as the latter.

(b) *Ordinary Portland cement*: Alumina-bearing material is added to the clinker to make up deficiencies in the alumina contents of other raw materials for the cement. Generally low-cost materials like clay and laterite are preferred. But if more alumina is required, then bauxite is used. Further, bauxite facilitates control of the alumina composition and moisture in the raw material mix due to its chemical homogeneity and low moisture-content as compared to clay or laterite.

14. Desiccation: For this purpose, activated bauxite and activated alumina are used. Activated bauxite is a low temperature (400°C) calcination product of gibbsite which is a tri-hydrate. Instead of gibbsite, Bayer's aluminium hydroxide which is also a tri-hydrate, but purer than bauxite can also be used, and in that case, the product is called "activated alumina". The temperature is enough to drive off only 2 of the 3 water molecules. Consequently, the material does not shrink completely, and the product is porous with large and active surface area. Since the dehydration is a reversible process, these products can recombine with water rapidly, and are useful for drying air, various gases and organic liquids.

15. Petroleum refining and fertilizer manufacture: In this application activated alumina (as described above) is used. Highly pure activated alumina has the ability to withstand thermal and mechanical shocks. This property of activated alumina combined with its large surface area with enhanced reactivity enable it also to adsorb sulphur-and fluorine-bearing gases in petroleum fractions during refining and in fertilizers during their manufacture.

16. Catalyst and catalyst support: A catalyst should possess strong adsorbing ability so that the adsorbed material can be recovered easily leaving the catalyst intact. A catalyst support should be an inert substance meant for acting as a carrier for a catalyst, and it should not react with the catalyst while at the same time, should be able to resist chemical attacks and thermal shocks of the reactions that the catalyst may be engaged in.

Activated alumina (as described under serial number 14) is an excellent adsorbent of gases due to its high porosity, and it serves as a catalyst in the processes of (i) recovery of sulphur from H₂S gas extracted from the exhaust gases released during refining of natural gas, (ii) removing excess water from alcohol and making it available again after synthesis of alcohol with the help of water, and (iii) isomerization of olefin.

Calcined alumina, by virtue of its inertness and resistance to both chemical attack and thermal shock, is used in the form of pellets or powder incorporated in matrices of certain catalysts. Examples of such catalyst systems are (i) platinum-palladium catalyst supported on calcined alumina, used in catalytic converters for automobiles to oxidize unburnt hydrocarbons and carbon monoxide that are hazardous, to harmless carbon dioxide and water; (ii) dehydrogenation catalyst for synthesis of olefins; (iii) platinum-based catalyst used in petroleum refining to yield high-octane antiknock gasoline; (iv) cracking catalyst, incorporated in silica-alumina matrix, used in petrochemical industry.

17. Pig iron and steel manufacturing: The most important function of bauxite in both pig iron and steel manufacturing is to control the volume and fluidity of the slag. Both alumina and silica contribute to the volume and fluidity of the slag in the blast furnace and the steel melting shop, and the individual value of Al₂O₃ as well as the Al₂O₃/SiO₂ ratio are crucial for this purpose. Too low a slag volume in the furnace is not conducive to efficient absorption of sulphur that may go into the furnace through coke and too high a volume affects productivity of the furnace and creates handling

problems. Besides, alumina-content in the slag assumes added importance if the slag is meant for manufacturing slag cement (for this purpose, slag should generally contain 12-16% alumina).

Although alumina has a high melting point and it requires more heat to melt and become fluid, some alumina along with silica is desirable for achieving an optimum level of slag volume so as to facilitate absorption of the sulphur. So, ideally, there should be an optimum $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in the raw material mix. Generally, in India, it is endeavoured to keep the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio at 1.5-3.0, although, a ratio of 1-1.5 is considered ideal and desirable. To adjust this ratio, sometimes a little extra alumina needs to be added to the mix. Since a little alumina does not require too much heat to melt, the fluidity of the slag can be maintained without incurring much cost—particularly if the alumina is added in the form of bauxite which is a cheap material (vide also the chapter “Iron Ore—Hematite”, specifications for pig iron).

Thus, bauxite serves the triple purpose of maintaining fluidity and volume of the slag, desulphurizing the iron/steel, and adjusting alumina-content of slag meant for slag cement.

For de-oxidation purpose, some quantities of aluminium metal is also added, because of its strong affinity for oxygen. The resultant aluminium oxide goes into the slag.

18. Plastics: Plastics are essentially resins. In this application, aluminium hydroxide is used. Its endothermic decomposition, and the high thermal conductivity and insulating property of alumina are the principal criteria. Aluminium hydroxide finds use as

- (i) filler in polymer systems
- (ii) synthetic marble

When aluminium hydroxide is used as a filler, it is added to plastics to serve three purposes i.e., (a) to economize on the quantity of resins by adding bulk, and/or (b) to impart electrical insulation property of the product, and/or (c) to make the product flameproof. In the latter case, flame decomposes the hydroxide, and the released water molecules not only absorbs the heat and cools the flame, but also dilutes the inflammable gases and oxidant in the flame. In addition, the residual alumina, being a good thermal conductor, quickly transmits the heat from the burning plastic.

Synthetic marble is a combination of very finely ground (below 60 mesh) aluminium hydroxide (50-85%), solvent for resin (5-16%), and the balance some thermosetting resin (e.g., polyester, acrylic). The pasty mixture is moulded into desired shapes and sizes before setting by application of heat or some catalyst. Synthetic marble may be translucent or opaque depending on whether the aluminium hydroxide is coarse-grained or fine-grained, and its colour depends on the purity of the hydroxide. It has fire-retardant property and suitable for use in bathrooms and structural components.

19. Ceramics: In high alumina ceramics, finely milled calcined alumina is used to the extent of 85.0-99.9 per cent. Particle preparation is very important for obtaining high packing densities, and is done by different methods including communion, precipitation, atomization, vapour deposition, thermal quenching. The particles are then formed into the desired shapes. Since alumina is not a plastic substance, special techniques are deployed for forming, such as:

- (i) Cold forming processes which include die casting, extrusion, plastic forming with organic aids, impacting etc.
- (ii) Hot forming processes in which the cold forming operations are performed under high temperature (up to 2200°C) and high pressure (up to 40000 psi), often combined with sintering and rolling into plates and sheets.
- (iii) Melt forming processes which include fibre drawing, fusion casting etc. (cf. glass technology).

High alumina ceramic objects are able to resist wear resistance at temperatures of 1650°C and above. Depending upon the usage, magnesia, graphite, lime and silica are added to alumina before forming. In the electronic industry, alumina ceramics are used as inert substances in base of circuitry, in sealed packaging for semiconductor microcircuits, in radio frequency transmitting valve envelopes, in transistor housing etc. In iron and steel industries, high alumina ceramic crucibles and tea pot ladles are used for special melting trials and for molten metal transfers respectively. Other applications include automotive spark-plug insulators and high voltage insulators. In pottery, calcined alumina is added to enhance whiteness, opacity, strength and chip resistance of wares. It is also added to glazes.

With a view to improving fracture toughness of alumina ceramics, zirconia is added by dispersing it in an alumina powder matrix, compacting the mixture and sintering at 1500-1600°C. Zirconia-toughened alumina ceramics find use in a variety of mechanical applications that include cutting tools, wear-resistant components (bearings, valves, wire drawing dies etc.), rocket radomes, hip joint prosthetic devices, tooth and ear implants, armour plating, bullet-proof vests, coin-polishing assemblies etc.

20. Proppant in oil wells: If there are fracture zones in the rocks of a petroleum or natural gas reservoir, then the rocks tend to cave in and block the wells adversely affecting the recovery. Proppants are materials which are used for filling up the fracture cavities to prevent closure of the wells, but without reducing the permeability of the reservoir rock, so that flow of oil or gas can be sustained. Although, quartz or silica sand is used in wells up to 3000 m deep, it is not strong enough to be suitable beyond this depth. In case of such deep-seated reservoir rocks, fine grains (less than 12 micron size) of calcined and sintered bauxite are used. Bauxite is sintered at 2000°C. Calcination produces ultra-fine crystals of alpha alumina, which are much harder (9 in Mohs scale) compared to quartz (7 in Mohs scale). Sintering makes the grains angular. The haphazardly-sized angular grains serve to make the fillings permeable, and any clay mixed with these grains is strictly objectionable as it blocks the pore spaces.

21. Welding flux: The definition and mechanism of welding have been described under “Uses” in the chapter “Iron Ore—Hematite”. Of the different types of welding, the most common is arc welding, and “*shielded metallic arc welding*” is an arc welding process in which the joining of the metals is accomplished by melting the parent metal and the tip of a flux-coated electrode. An electric arc between the electrode and the work provides the heat (around 6000°C temperature). The purpose of flux coating is to

- (i) clean the work by fluxing impurities into the slag,
- (ii) provide a gaseous shield for the weld while molten,
- (iii) form a protective cover of slag over the weld to shield it during solidification and cooling,
- (iv) de-oxidize the weld, reduce porosity, and improve neatness,
- (v) stabilize the arc and minimize spatter,
- (vi) help shape the bead and give better penetration.

In one of the types of shielded arc welding, the flux material contains calcined bauxite. Its alumina and silica contribute to slag formation. The calcined bauxite should be free from phosphorus and sulphur which make the weld brittle. If any residual water remains in the calcined bauxite, the same should not be more than 0.5%, because the arc reduces it releasing hydrogen, which, if absorbed by the molten weld, makes the latter brittle.

22. Road aggregate: Most road aggregates (e.g., limestone, flint, quartzite), over a period of time, tend to become polished due to abrasion under traffic load, and as a result, vehicles become

susceptible to skidding. Crystalline grains of calcined alumina (1-3 mm size), due to their hardness (9 in Mohs scale), serve as a good additive to prevent polishing and to impart anti-skidding property to road surface. It prolongs the skid-resistance by up to 10 times in comparison to an average road aggregate. It is applied after coating the surface with epoxy resin for good bonding. But, because this is an expensive material, it is applied to the road surface only at selected locations such as accident-prone points, sharp curves, intersections etc.

23. Paper: Aluminium hydroxide of a high degree of purity is used as a coating substance to enhance brightness, opacity and smoothness of paper. It is particularly preferred as a partial substitute of china clay or titanium dioxide for paper boards where, in addition to these properties, strength is also a criterion.

24. Rubber: In this application, aluminium hydroxide is used. Its endothermic decomposition, and the high thermal conductivity of alumina are the principal criteria. Aluminium hydroxide finds use as a filler. Aluminium hydroxide is added to rubber to make the product flameproof. Flame decomposes the hydroxide, and the released water molecules not only absorb the heat and cool the flame, but also dilute the inflammable gases and oxidant in the flame. The residual alumina, being a good thermal conductor, quickly transmits the heat from the burning rubber.

25. Adhesives and sealants: To adhesives and sealants used in construction works, aluminium hydroxide is added as filler mainly for improving their strength and life and also for reinforcing the binder.

26. Ball mill grinder: Pieces of calcined alumina are used in special types of ball mills for grinding very hard substances. The high value of hardness (9 in Mohs scale) is the main criterion.

27. Artificial cordierite: A comparatively recent development is a material called "*cordierite saggars*", made from artificial cordierite. Saggars are trays used as kiln furniture and shelves for firing powders or components in porcelain and ceramic manufacturing. Artificial cordierite has the composition $Mg_2Al_4Si_5O_{18}$. It has the same characteristics as natural cordierite, which is formed due to contact metamorphism. It crystallizes above 950°C and remains stable over a considerable range of temperature i.e., up to 1750°C. It has low linear expansion, low coefficient of thermal expansion, excellent resistance to thermal shock, high mechanical strength, ability to work in both oxidizing and reducing atmospheres and to withstand rapid temperature changes without breakage. Saggars made of artificial cordierite have long lives of 10-15 firing cycles. Artificial cordierite can be derived from an admixture of clay, grog, bauxite powder and talc.

SPECIFICATIONS OF USE

The specifications of bauxite are related to both processing technology and end products besides costs. The main end-uses of bauxite described in the preceding section can be grouped into the following 8 groups from the point of view of direct use of bauxite as such:

1. Bayer's process for producing aluminium hydroxide: This is the base for manufacturing (i) alumina (its downstream utilities are aluminium metal and metal-based products; ceramics; calcined alumina for use as refractories, catalyst supports and ball mill grinder; sintered alumina for use in refractories; white fused alumina for abrasives), (ii) some chemicals (e.g., aluminium nitrate, chloride and fluoride), (iii) soft abrasives, (iv) seeded alumina gel abrasive, (v) adhesives and sealants, (vi) activated alumina for use in petroleum refining, fertilizer manufacture, and some types of catalyst, (vii) paper coating, (viii) flame-retardant plastics and rubber.

2. Low temperature calcination for making activated bauxite: This is used for desiccation.
3. High temperature calcination for making calcined bauxite: This is the base for making (i) refractories, (ii) sintered bauxite (used in refractories and as proppant in oil wells), (iii) road aggregate, (iv) welding flux.
4. Fusion for making brown fused bauxite: This is used in abrasives.
5. Digestion with sulphuric acid and caustic soda to make some types of chemicals (e.g., aluminium sulphate, alums, and sodium aluminate).
6. High-alumina cement.
7. Ordinary Portland cement.
8. Pig iron and steel.

The specifications relating to these eight direct uses of bauxite will now be discussed.

1. Bayer's process for producing aluminium hydroxide: Although Bayer's aluminium hydroxide is used to make a host of products including aluminium metal, the grade of bauxite used for its manufacture is generally referred to as *metallurgical or metal grade*, because almost 90% of it goes into aluminium industry — particularly in India. Nevertheless, the principle of the specifications is process-specific, and is the same irrespective of the purpose for which this aluminium hydroxide is used. The criterion is digestibility of the bauxite in caustic soda as economically as possible. Caustic soda is the costliest of the input materials, and its consumption per tonne of alumina contained in the bauxite varies from 78-131 kg, which is called the "*molar ratio*". Another cost-intensive part of the process is the disposal of the solid waste material called "*red mud*". The aim, therefore, is to digest maximum quantity of bauxite with minimum consumption of caustic soda to produce aluminium hydroxide of the highest purity with minimum generation of red mud. The principles underlying the specifications with regard to the different parameters are as follows.

- (a) *Mineralogy*: From the point of view of digestibility in caustic soda, gibbsite, being the softest of the three minerals, is the most suitable, followed by boehmite, both of which are products of weathering. They can be digested at relatively low temperature in low-concentration caustic soda. Diaspore, which is a product of metamorphism, is the most difficult to digest. So, bauxite with gibbsite content as high as possible and the lowest possible diaspore content, is preferable.
- (b) *Alumina*: Alumina percentage need not necessarily be high. What is important is a low molar ratio (caustic/alumina). Theoretically, gibbsite contains 65.35% alumina compared to 84.98% each in boehmite and diaspore. So, a predominantly gibbsitic bauxite (which is preferable) is likely to contain less alumina than the one containing a mixture of gibbsite and boehmite. But, since the objective is to extract the alumina value of the bauxite, its highest possible content is desirable, subject, of course, to a favourable mineralogy and availability at an economical price.
- (c) *Silica*: This occurs in bauxite in two forms – reactive and non-reactive. Reactive silica comes from clay and other silicates, in which it remains in chemical combination. Non-reactive silica is the free silica (quartz). The former is considered to be more objectionable than the latter.

The reactive silica goes into solution in the sodium aluminate liquor, formed after digestion of bauxite in caustic soda, and reacts with a part of the sodium aluminate to form sodium aluminosilicate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) from which aluminium hydroxide cannot be

precipitated and which has to be discarded, thus causing loss of both soda and alumina. Approximately, 1.1 units of alumina and 1.2 units of soda are lost for each unit of silica in the ore.

Non-reactive silica, being hard, adds to the grinding cost of the bauxite, and it goes into the red mud. Thus it adversely affects the overall economics.

- (d) *Iron and titanium oxides:* Fe_2O_3 and TiO_2 are not positively harmful, but they form the insoluble red mud and add to the costs.
- (e) *Phosphate and carbonates:* Like silicates, these are also partly soluble in caustic soda, and they result in loss of soda effectively available for digestion of bauxite. They are finally precipitated as sludge when, after digestion process is complete, the residual sodium aluminate liquor is concentrated by evaporation. This sludge also adds to the solid waste. So far as Indian ores are concerned, the carbonates (calcite, dolomite and siderite) are not a problem.
- (f) *Organic matter, vanadium and gallium:* Organic matters are sometimes present in bauxite, and also are introduced into the plant liquor from the flocculating reagent when the latter is added to the slurry of liquor and red mud in order to separate them. Vanadium and gallium are present in some ores – in India as well as elsewhere. In course of time, the organic impurities build up in the liquor in the form of oxalates, humic acid, vanadates, gallates etc. While vanadium and gallium are recovered as byproducts, the first two of these organic compounds are harmful, because they give rise to foaming effect with reduction of heat transfer efficiency. Organic compounds can be removed by wet oxidation process, which also adds to the cost.
- (g) *Water molecules:* This is represented in terms loss on ignition (LOI) at a standard temperature (1100°C). If the type of bauxite (trihydrate gibbsite or monohydrate boehmite) is fixed, then LOI becomes automatically specified. It is an indicative of the type of bauxite, and more it is the better.

The Bureau of Indian Standards (BIS), in 1985, has set a standard of specifications for different parameters. By and large it is: *minimum total Al_2O_3 : 40% for gibbsitic bauxite and 47% for mixed gibbsite-boehmite-diaspore bauxite; total SiO_2 : 4% (max); $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio : 12 (min); $\text{Fe}_2\text{O}_3+\text{TiO}_2$: 30% (max); P_2O_5 & V_2O_5 : each 0.2% (max); LOI: 20% (min)*. Most of the Indian bauxite ores are predominantly gibbsitic, and the Indian industries generally use ores containing 42.5-49.0% or more Al_2O_3 ; 1.65-3.50% reactive silica; 20-30% $\text{Fe}_2\text{O}_3+\text{TiO}_2$.

2. Low temperature calcination for making activated bauxite: In this case, the objective is to achieve maximum pore space. If the bauxite consists of monohydrate boehmite, then the mass shrinks and becomes compact when the only water molecule is removed, because there will be no more water to absorb the heat. Therefore, only trihydrate gibbsitic bauxite is suitable. Enough pore space is left after expulsion of two water molecules, and still one water molecule will be left to absorb heat and prevent shrinkage.

3. High temperature calcination for making calcined bauxite: It is generally referred to as *refractory grade bauxite*, because that industry is the most dominant consumer of this grade. Calcined bauxite for use in good quality refractories should contain more than 88% Al_2O_3 , 2.5% (max) Fe_2O_3 , 4% (max) TiO_2 , 7% (max) SiO_2 and very low alkalis. A typical Guyana refractory-A grade super-calcined bauxite contains 88.3% Al_2O_3 , 1.75% Fe_2O_3 , 3.2% (max) TiO_2 , 6.5% (max) SiO_2 and 0.25% LOI.

For calcination, low water content means less requirement of heat, and hence, monohydrate boehmite and diasporite are preferred to gibbsite. Monohydrates also ensure a high content of alumina, which is obviously desirable as all the end-use products contain high alumina. However, in India, gibbsitic bauxite being predominant, the same with as high the contents of boehmite and diasporite, as may be available economically, is used.

Fe_2O_3 and TiO_2 are both deleterious because at the high temperature in furnaces where the refractory products are used, they form low-melting iron-titanate glass causing blisters in the refractory bricks and consequent increase in porosity. SiO_2 is also objectionable because of its differential thermal expansion that causes cracks in the bricks. Alkalis and lime lower the fusion temperature, and hence are deleterious. Very low percentages of these impurities automatically ensure a very high percentage of alumina.

Particle size should be within an optimum range. More than 50 μm size causes incomplete calcination, while smaller than 100 micron tends to create dust problem.

The BIS, in 1984, has specified 58% (*min*) Al_2O_3 , 3% (*max*) Fe_2O_3 & TiO_2 each, 0.5-0.6% CaO , and 27-30% *LOI*. The Indian industries, however, are known to use bauxite containing lower Al_2O_3 (54%), and higher values of Fe_2O_3 (5%) and CaO (1%). Even bauxite containing as low as 45% Al_2O_3 has been found feasible to use provided $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio is at least 5, SiO_2 and TiO_2 are not more than 4% and 0.3% respectively. Malaysian and Brazilian gibbsitic bauxite of this grade contains 59% Al_2O_3 , 2.8% Fe_2O_3 , 0.4% TiO_2 , 7.7% SiO_2 and 30% *LOI*.

4. Fusion for making brown fused bauxite: This is also referred to as *abrasive grade* bauxite, because this intermediate product is used for making some types of abrasives. Ultimately it is the alumina transformed to hard corundum grains that constitutes the abrasive product, hence this constituent in the raw bauxite becomes the most critical. Also, excess water leads to explosive generation of superheated steam at the very high fusion temperature, and water-content in the bauxite, therefore, should be minimum. These two criteria together make monohydrate bauxite preferable.

Fe_2O_3 and SiO_2 —both are deleterious. These oxides have to be reduced by coke to form Fe-Si slag which then has to be magnetically separated. Their excess presence increases the coke consumption and operational cost of the process. Also, if the reactive silica component (in the form of silicates) in the total silica alone is in excess, then it cannot be removed by this process as it forms mullite (aluminium silicate) causing loss of alumina as well as inhibiting corundum formation, and the overall hardness and quality of the abrasive product suffer. On the other hand, if the non-reactive silica component (in the form of free silica) is in excess, it is possible that the Fe_2O_3 present is not sufficient to remove it completely, and additional iron pieces have to be added. So, reactive silica, total silica, and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratio – all should be low.

Excess TiO_2 is deleterious because at the high temperature it combines with Fe_2O_3 to form low-melting iron-titanate glass, causing the bauxite to fuse at a lower temperature inadequate to form the alpha structure of corundum. Moreover, this also consumes some Fe_2O_3 making less of it available for removal of silica. However, TiO_2 alone being infusible at the fusion temperature of bauxite, a little of it is desirable for preventing the latter from fusing at a lower temperature due to some of the other impurities. An optimum range is, therefore, specified.

For the same reason, the alkalis which form low melting glass with silica and thus inhibits formation of corundum structure, are highly objectionable. Lime is also highly deleterious, as it lowers the fusion temperature of bauxite.

The particle size (for the same reason as for refractory manufacture) should neither be too small nor too large.

There is no BIS specification for this use of bauxite. Industries adjust their process designs according to availability of bauxite keeping in view the overall economics of production. In some countries, industries demand bauxite containing 80% (min) Al_2O_3 , 7% (max) total silica, 3:1(max) $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratio, 0.1% (max) CaO, 1.0% (max) LOI, 2-4% TiO_2 , and 100 micron to 50 mm particle size. The industries in Greece use a different grade with 56-60% Al_2O_3 , 1.5-3.5% total silica, 22-24% Fe_2O_3 , 0.4% (max) CaO, 0.9% (average) alkalis, and 2.9% (average) TiO_2 . The bauxite ores used by Indian industries contain 45-60% Al_2O_3 , up to 1% reactive silica, 1.5% non-reactive silica, 22-27% total iron oxides, 3% Fe_2O_3 , up to 0.9% CaO, 25-30% LOI, up to 3% TiO_2 .

5. Digestion with acids to make some types of chemicals: It is generally referred to as *chemical grade* bauxite. Since, the processes involve digestion of bauxite in acids (for the sulphate and the chloride) or caustic soda (for the sodium aluminate), and since gibbsite is more easily digestible, gibbsitic bauxite is preferred. At the same time alumina, being the main component in the products, should be as high as possible.

Fe_2O_3 and SiO_2 are the most critical impurities in the Indian context. Fe_2O_3 is soluble in acids, but insoluble in caustic soda. So, when bauxite is digested in acids for sulphate and chloride production, a portion of Fe_2O_3 also goes into solution and remains in the product, affecting its colour and purity. Ideally, $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio of 100:1 is desirable; but if the sulphate is meant for use as a flocculating agent in treatment of water and effluents, then higher iron is acceptable as it does not affect the flocculating efficiency. When bauxite is digested in caustic soda for sodium aluminate production, Fe_2O_3 precipitates and adds to the bulk of the solid wastes and increases the cost of removal and disposal.

As regards SiO_2 , it tends to form gel, and its excess creates difficulties in settling and filtering, and also hinders chemical reactions. When silica is in silicate form, it forms sodium aluminosilicate in the process of digestion in caustic soda, and results in loss of both alumina and costly soda.

TiO_2 is not directly harmful, but it forms the insoluble waste material and adds to the costs. Phosphate and carbonates, like silicates, are also partly soluble in caustic soda, and result in loss of soda effectively available for digestion of bauxite. They are finally precipitated as sludge when, after digestion process is complete, the sodium aluminate liquor is concentrated by evaporation. This sludge also adds to the solid waste. So far as Indian ores are concerned, the carbonates (calcite, dolomite and siderite) are not a problem. Manganese oxide, like Fe_2O_3 , is soluble in acids and insoluble in caustic soda. So, in production of the sulphate and the chloride, it affects their colour and purity, whereas in sodium aluminate production, it precipitates and adds to the solid waste and cost.

The BIS, in 1984, has specified : 58% (min) Al_2O_3 , 2% (max) Fe_2O_3 , 3% (max) SiO_2 , 4% (max) TiO_2 , 0.3% (max) P_2O_5 , 0.1% (max) MnO , 0.2% (max) $\text{CaO}+\text{MgO}$. The Indian chemical industries actually use somewhat lower grade bauxite containing 50% (min) Al_2O_3 , 5% (max) Fe_2O_3 , (+) 3% total SiO_2 , 6% (max) TiO_2 , 0.6% (max) CaO.

6. High-alumina cement: The composition of the product being mono-calcium aluminate, it is important that Al_2O_3 and CaO should be in the right proportion in the bauxite. An $\text{Al}_2\text{O}_3/\text{CaO}$ ratio between 0.85 and 1.30 is considered to be most suitable.

So far as the other impurities of bauxite like Fe_2O_3 and SiO_2 are considered, they are not critical for most uses. The former affects the refractoriness where it is used in refractory lining, and the latter affects the rapid-setting property to some extent.

For high iron aluminous cement, users generally prefer bauxite with an $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ of 2.0-2.5:1 and an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of up to 10:1. For low-iron type, the industries' specifications are $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio 20:1, $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio 16:1, and SiO_2 max 6 per cent. In both cases, moisture should be minimum as it affects heat economy of the manufacturing process, and Al_2O_3 should be in the region of 50-60 per cent.

7. Ordinary Portland cement: Some aluminous material may be required to be added to adjust the silica modulus i.e., $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ in the raw material mix, which should be 2.6-2.8. The degrees of deficit or excess of these constituents and the cost determine the choice of the additive amongst clay, laterite and bauxite.

8. Pig iron and steel: The purpose may be either adjusting the volume and fluidity of the slag for efficient absorption of phosphorus and sulphur, or for making the slag suitable for manufacturing slag cement, or both. There is no standard specifications, which depends on the composition of the other raw materials and of the slag produced.

For pig iron and steel manufacturing, some Indian industries use bauxite containing 50-60% Al_2O_3 , up to 6% SiO_2 , up to 14% Fe_2O_3 , up to 9.6% TiO_2 , up to 1.0% $\text{CaO} + \text{MgO}$, up to 0.05% P and 20-30% LOI. In some other countries, the industries prefer monohydrate boehmite and diasporic lumps (10-50 mm size) containing low moisture, a minimum of 55% Al_2O_3 , up to 7% SiO_2 , and trace P + S.

So far as addition of bauxite for only making the slag suitable for cement is concerned, Al_2O_3 and SiO_2 are the most important parameters. Ideally, slag should contain 12-16% Al_2O_3 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio close to 2:1. On an average the Al_2O_3 content of slag in North America is 8%, and that in India is 26 per cent.

WASTE UTILIZATION

Wastes may be in all the stages starting from in situ deposit through processing to the final product. These are discussed as follows.

1. In situ stage: As the reserves of high grade bauxite are getting depleted or are inadequate in many countries – particularly developed ones, greater attention is being directed towards development of technologies for use of low grade bauxite. Bayer's process categorized as "alkali process" is not suitable for treating such ore of bauxite, and for these ores different technologies have been developed and tried, besides beneficiation.

- (a) *Beneficiation:* For use of bauxite in nonmetallurgical industries by calcination as well as for use in Bayer's process, beneficiation may be necessary. The impurities in bauxite are generally so finely dispersed that their removal by physical methods of ore dressing is seldom met with success. Sand and clay may be washed and screened and iron may be reduced by magnetic or gravity separation. However, the concentrates produce being very fine grained, are not suitable for calcination.
- (b) *High silica bauxite:* This type of ore is unsuitable for processing by Bayer's process for extraction of aluminium hydroxide, because reactive silica causes loss of both soda and aluminium while non-reactive silica adds to the bulk of solid waste. A process was developed for treating such bauxite. It consisted in sintering the material with limestone to fix the silica as di-calcium silicate, and then treating the product by Bayer's process. But the additional treatment would add to the cost of extraction, and was not found economically feasible at the prevailing price of the product.

- (c) *High iron bauxite*: The high iron bauxite is first smelted with limestone, by which calcium-aluminium slag and cast iron are produced. The slag is then leached with Na_2CO_3 yielding sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$), which is then processed further as in the Bayer's process. This is a costly process, but was used in Russia and Norway during World War-II.
- (d) *Low grade aluminous clay*: The processes being tried include (i) carbothermic process, (ii) Toth process and (iii) Kuwahara process. All these processes bypass the Bayer's route altogether. In carbothermic process, the alumina of the clay is reduced with carbon. The aluminium carbide produced is separated from clay, decomposed at 2100°C and below atmospheric pressure, and is reduced to aluminium. The Toth process developed in USA, consists in calcination of the clay, feeding the fine grained calcined clay to a fluidized bed reactor, and then chlorination, yielding aluminium chloride which is reduced to aluminium by manganese.

In the Kuwahara process developed in Japan, the clay containing as low as 35% Al_2O_3 is mixed with coal, finely ground, briquetted, and then heated in a coking furnace to $600\text{-}900^\circ\text{C}$ in an inert gas. These 'coke briquettes' are heated in a furnace by electric arc to 2000°C , yielding an alloy containing 60% Al and 40% Fe, Si and Ti. By spraying molten lead in the furnace at 1200°C , the Fe, Si and Ti are separated and an aluminium-lead alloy is produced, which is then liquefied in a pot. The heavy lead settles at the bottom and aluminium floating at the top is recovered. This somewhat impure aluminium containing about 1% lead is purified by fractional vacuum distillation.

2. Processing stage:

- (a) *Bayer's liquor*: The residual sodium aluminate liquor, after precipitation and extraction of aluminium hydroxide, contain valuable caustic soda. This is partly recovered and re-circulated into the process, thus saving on the cost of this chemical. The recovery of caustic soda from the waste liquor is by evaporation.
- (b) *Vanadium and gallium*: Small amounts of vanadium and gallium present in bauxite, find their way into Bayer's liquor during extraction of aluminium hydroxide. These elements beyond a certain limit, in the re-circulating liquor, start contaminating the product aluminium hydroxide, and hence it becomes essential to continually purge them out from the liquor. Moreover, these elements are metals of economic importance. It has become an established practice the world over to recover vanadium and gallium as byproducts from Bayer's process, wherever feasible.
- (c) *Red mud*: Red mud is the solid waste generated in huge quantities from Bayer's process. Its other names are "*residual bauxite*" and "*ferro-alumina*". It comprises mainly the iron oxide and titania that are present in the bauxite raw material, along with some alumina and adherent caustic soda. This is a major source of pollution in alumina plants and poses several problems in its disposal due to the presence of the caustic soda and requirement of large areas for constructing storage ponds. According to some rough estimates, about 50 million tonnes of red mud are generated in the world annually. At present technologies are available for its utilization in cement and plastic industries and also for manufacturing pig iron. Intensive research and development activities are in hand in different countries including India for making other products like bricks and pigments, and recovery of titanium.

3. Product stage:

Scrap: Scrap is generated right from the stage of smelting of aluminium to the final stage of consumer products. Dross, spalls and spills (collectively termed in trade circle as “*thril*”) generated in the smelting furnace when the metal is still in molten state, and used utensils, consumables etc. – all constitute the aluminium scrap. Utilization of aluminium scrap signifies an additional metal supply supplementing the primary production. Moreover, recycling of aluminium saves up to 95% of the power and the entire cost on account of the other input materials including caustic soda.

Aluminium scrap can be recycled practically endlessly compared to 11 years life span of wood (7 times heavier than aluminium) and 20 years life span of steel (2.8 times heavier than aluminium). Typical life cycles of different aluminium products are:

<i>Product</i>	<i>Life cycle (years)</i>
Conductor and cables	35
Building	40
Transport	7
Packaging	1
Consumer durable	10
Utensil	3
Castings	20

But the problem lies in the efficiency of collection of scrap. The world average recycling rate is around 23%, the major countries being Japan (40%), Europe (40%), USA (35%), Canada (33%) and India (20%). The most important consumers of recycled aluminium in India, are the utensil, steel and foundry industries, while in USA, canning industry is the most important consumer (the average beverage cans are made of more than 51% recycled aluminium).

SUBSTITUTION

1. Bauxite by non-bauxite ore: As the reserves of high grade bauxite are getting depleted and have become inadequate in many countries, greater attention is being directed towards development of technologies for use of non-bauxite sources of alumina. The only non-bauxite ores used today on a large scale are nephelene [$\text{Na}_8\text{K}_2\text{Al}_8\text{Si}_9\text{O}_{34}$] and alunite [$\text{K}_2\text{Al}_6(\text{OH})_{12}(\text{SO}_4)_4$, aluminium content 37%] in Russia.

2. Aluminium metal by other material: Aluminium itself has substituted copper, steel and other materials in a number of industrial applications due to its superior properties in many respects and short and long term cost advantages. However, aluminium, steel, copper and plastic can be used interchangeably depending on the specific performance criteria.

CHROMITE

Chromite is an oxide of iron and chromium having chemical composition $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and belonging to the spinel group. It is the only commercially exploited ore of chromium, and is also referred to as “chrome ore”. Theoretically it contains 46.5% Cr and 25.8% Fe with Cr/Fe ratio 1.8:1. But in nature, the ferrous iron is generally replaced partially by magnesium, and the chromium by ferric iron or aluminium, with consequent variations in the Cr/Fe ratio. Thus, its composition is represented by the generalized formula $(\text{Fe}, \text{Mg})\text{O} \cdot (\text{Cr}, \text{Al}, \text{Fe})_2\text{O}_3$. It occurs in ultrabasic igneous rocks generally associated with peridotite, pyroxenite, serpentinite and dunite. Its commercial deposits are broadly of two types – podiform and stratiform. The former is generally high-alumina and the latter iron-rich.

HISTORY

Chromite was first mined in Norway in 1820 as a refractory material. In 1903, its mining commenced in Beluchistan, Pakistan, followed in Mysore and Singbhum districts, India in 1907 and 1909 respectively. But the most famous and the largest resources of Orissa state were discovered only in 1943. During the 44 years period from 1903 to 1946, the cumulative total production in the states of then India (i.e., including present Pakistan) was 1.4 million tonnes, out of which about 0.74 million tonnes were in the states belonging to present India. The production reached the peak figure of about 62000 tonnes in 1937, and thereafter, during the five-year period 1942–1946, averaged only 24000 tonnes per year. In India, since independence in 1947, the production profile of chromite was as follows.

1950	17000 tonnes
1960	107000 tonnes
1970	274000 tonnes
1980	321000 tonnes
1990	959000 tonnes
April, 2000–March, 2001	1.97 million tonnes

During the year 2000, the world production stood at 14.6 million tonnes, and India ranked third after South Africa and Kazakhstan.

CRITERIA OF USE

- (1) **Chemical composition:** Amongst all natural minerals, chromite contains the highest percentage of chromium, and it is naturally associated with iron. But more important, it usually occurs and is mined not in its chemically pure form, but in altered forms wherein Cr/Fe ratio becomes higher than the theoretical ratio of 1.8:1.
- (2) **Chemical affinity:** Chromium forms a number of chemical compounds.
- (3) **Chemical neutrality:** Chromite is nearly neutral from chemical standpoint. It is practically insoluble in both basic and acidic slags.
- (4) **Chemical form:** Chromium may have valencies 2, 3, 4, 5 and 6. But in chromite it is in trivalent form (Cr-3), and in some of the deposits it contains *hexavalent chromium* (Cr-6). Both these forms of chromium take part in chemical and industrial processes, but some amounts of them may get released from the chrome ore.
- (5) **Fusion temperature:** Softening temperature of commercial chromites varies from 1250–1450°C. The fusion temperature of pure chromite is 2180°C, but that of the commercial ones as found in nature, varies from 1700–1900°C. The variations in the softening and fusion temperatures depend on the content of iron in particular and also on the impurities like silica, increases in their contents resulting in decreases in these temperatures. The fusion temperature of chromium metal is also very high –1907°C.
- (6) **Physical form:** In nature, chromite occurs both as hard compact and lumpy ore and as friable and powdery ore depending on the tectonic history of the deposit.
- (7) **Physical properties:** Chromium metal is highly resistant to corrosion due to a tenacious film of chromium oxide on the surface, has a bright shining metallic lustre, and it takes an excellent polish. The reflecting power of a polished chromium is 77% that of silver. Chromite is made up of coarse octahedral crystals, is brittle with medium hardness (5.5 in Mohs scale), and it breaks with uneven fracture.
- (8) **Mechanical properties:** Alloying of chromium metal with other metals improves hardenability, adds strength and imparts resistance to fatigue, creep, friction, impact, chemical attack, electrical and thermal shocks.
- (9) **Electrical properties:** Electrical conductivity of chromium is relatively low, being only 22.2% that of copper.
- (10) **Alloying ability:** Chromium readily alloys with a number of metals.
- (11) **Chilling effect:** The process of solid solution of pure chromium metal during alloying is endothermic, and produces a chilling effect.

USES

Chromite is used for manufacturing some intermediate as well as end products. Intermediate products are exclusively used to make some finished products, which, although not a direct derivative of chromite, has become too closely associated with it to be treated separately. The intermediate and end-uses of chromite are:

- A. Beneficiation
- B. Agglomeration
- C. Metallurgical

- (1) Ferrochrome
- (2) Stainless steel
- (3) Nickel chromium alloys
- (4) Other alloy steels
- (5) Chromium metal
- (6) Nonferrous alloys
- (7) Foundry
- (8) Chrome-plating
- (9) Metallization

D. Nonmetallurgical

- (1) Chemical
- (2) Refractory
- (3) Human health

These uses are elaborated as follows

A. Beneficiation: In India, although a chromite beneficiation plant was in operation in the 1970s, widespread commercial practice of beneficiation of low grade chromite is relatively recent, dating back to the 1990s. But it has made a drastic difference to the resource availability of chromite. Chromite concentrate is not an end product, but it is a tradable product in the domestic as well as international market. Typically, the technology is based on the principle of gravity separation. The friable and the fine-sized ores are crushed and ground to (–)150 micron size, and the beneficiation process consists of desliming in hydrocyclones, followed by spiraling and tabling. These processes serve to increase the Cr_2O_3 - content and reduce the SiO_2 - content, but no appreciable improvement in Cr/Fe ratio takes place. Magnetic separator may also be introduced in the circuit for treatment of ferruginous ores to improve Cr/Fe ratio. The low grade lumpy ores containing lots of clay that are not directly usable, are crushed and washed.

B. Agglomeration: The product of beneficiation i.e. the concentrate, is fine grained, and in conventional metallurgical processes these cannot be directly used. For that purpose concentrates and also the high grade natural fines, are agglomerated into briquettes, sinters, pellets and *sintered pellets*. Briquettes are made by pressing the fines with or without bonding material. This is the simplest and cheapest method of agglomeration, but in many cases, briquettes do not retain their shape under smelting conditions. Sintering is carried out by partial fusion of the corners of the grains, and fluxes (e.g. limestone) are generally added at this stage itself. Pelletizing involves mixing the fines with bentonite (bonding material), fluxing material and coke, and then subject the mixture to rotational motion in drum or disc. Sintered pellet is essentially a combination product of pellet and sinter, and is considered superior to the other agglomeration products. For manufacturing this product, green pellets are burnt to a temperature ranging from 1350–1450°C in a sintering furnace.

C. Metallurgical:

- (1) **Ferrochrome:** Taking advantage of the natural association of chromium and iron, ferrochrome – not metallic chromium is added to steel for making stainless steels and other alloys of chromium and steel. This is added to steel as an alloying metal for improving various properties like resistance to heat, corrosion and abrasion, as well as strength, hardness etc., and the physical and mechanical properties of chromium are taken advantage

of. The alloy steel products include low to high carbon steels including stainless steels and tool steels for ordinary level performances. Ferrochrome is classified into six types:

- (a) High carbon ferrochrome
- (b) Charge chrome
- (c) Silicochrome
- (d) Medium carbon ferrochrome
- (e) Low carbon ferrochrome
- (f) Exothermic ferrochromium

Except silicochrome, all the other four types differ from each other mainly by carbon content. These types are discussed as follows:

- (a) *High carbon ferrochrome*: The carbon-content in the high carbon ferrochrome is in the range of 4–8%, while the chromium - and silica-contents may vary from 60–70% and 1–2% respectively, although 64–66% Cr and 5.0–6.5% C are relatively more typical.

The conventional manufacturing process involves smelting in an electric arc furnace (EAF). Chromite (in the form of natural lumps or agglomerated products) along with coke and some slag-forming materials like limestone, dolomite etc. are charged into the furnace. Some silica and alumina-bearing materials like quartz, bauxite etc. are also added for balancing the composition and volume of the slag depending on need. Improvements in the process mainly by way of preheating the charge with a view to reducing power consumption and cost and to improving metal recovery has been carried out. The process is highly power-intensive, consumption of power being in the range of 4200–5000 kwh per tonne of the product. There is one more technology namely, the plasma arc smelting technology. Plasma arc furnaces are in operation in Sweden and South Africa. In this process, the heat is produced by plasma torches. Its advantage lies in its ability to use ore fines and noncoking coal, but its main disadvantage is the high requirement of electricity.

- (b) *Charge chrome* : Charge chrome is a very high carbon low grade ferrochrome. It is actually “*charge grade chromium*”, as it is in this form that chromium is charged into the furnace for stainless steel manufacturing since the development of highly effective decarburization technologies namely, vacuum oxygen decarburization (VOD) and argon oxygen decarburization (AOD). Its carbon-content, as in the case of high carbon ferrochrome, varies up to 8% – generally 6–8%, but the chromium content is below 60% and may be as low as 50%; silica is also high, 3–6 per cent. Decarburization is critically important in stainless steel manufacturing, because carbon combines with chromium to form chromium carbide thus robbing the stainless steel of a portion of the chromium added. The VOD and AOD technologies (see the chapter on hematite) achieve decarburization very effectively, and so, low-chromium charge chrome combined with a high degree of decarburization can yield the same grade of stainless steel as high-chromium ferrochrome with a low degree of decarburization. That is how charge chrome has become a cheaper option and popular after the advent of the new decarburization technologies. The process employed for its manufacture is the same as in the case of high carbon ferrochrome.

- (c) *Silicochrome*: Ferrochrome silicon or chrome silicide or silicochrome is both an intermediate product used in making low carbon ferrochrome and a final salable product for charging in alloy steel making. Silicochrome is a high-silicon low-iron low-carbon product. In effect, silicon takes the place of a portion of iron. Typically, it contains 35–41% Cr, 35–45% Si and 0.05% C.

It can be made by resmelting high carbon ferrochrome with silica and coke or charcoal. But the most common method of producing it is by smelting in an EAF of charge composed of chromite, silica and coke or charcoal. Since no lime is added, there is no slag, and the silica does not go to form silicate. In the first method, carbon of the high carbon ferrochrome and the coke is oxidized by the silica and the silicon goes into solid solution with chromium. In the second method, the coke reduces both the chromite and the silica, and the chromium and silicon form the silicochrome.

- (d) *Medium carbon ferrochrome*: The range of carbon is 1–4% and that of chromium 65–75 per cent. Simply by blowing oxygen through molten high carbon ferrochrome in a converter and reducing the carbon content, the desired lower range of carbon can be achieved.
- (e) *Low carbon ferrochrome*: This is used in making very high quality stainless and other alloy steels meant for special products like chemical-manufacturing and food-processing equipment, surgical instruments, cryogenic vessels, nuclear power stations, spaceship components etc. Carbon should be below 0.5%, and more commonly varies from 0.015–0.05%; chromium 65–75%; and silicon less than one per cent.

Low carbon ferrochrome can be manufactured by oxygen refining of high carbon ferrochrome and reducing its carbon content in multiple stages. But this process is expensive. The common method uses high-silicon low-carbon silicochrome and chromite as the starting materials. The principle essentially consists of smelting the chromite with lime in an open arc furnace producing a chromium-rich chromite/lime slag, and treating this slag with the low carbon high silicon silicochrome. The silicon of the silicochrome goes to react with lime of the slag to form calcium silicate slag, while the chromium of the silicochrome and that of the slag add up to increase the chromium content of the product i.e., low carbon ferrochrome.

- (f) *Exothermic ferrochrome*: Exothermic ferrochrome is used when the chilling effect of adding conventional ferrochrome to the molten steel is undesirable. One such product is composed of ferrochrome, a small quantity of ferrosilicon or silicochrome, and sodium nitrate. It is produced in both low and high carbon grades.

- (2) **Stainless steel**: Stainless steel has been dealt with in the chapter on hematite. Chromium is the key element in it. It is defined as an alloy steel containing more than 9% chromium – with or without other elements. It is characterized by a high degree of resistance to corrosion or oxidation or rusting. In ordinary steels, the initial oxidation forms a loose permeable scale which holds moisture and allows oxygen to diffuse readily and progressively attack the metal below. In contrast, in stainless steels, the initial oxidation forms a very thin, transparent and highly adherent skin of chromium oxide which, being impervious to oxygen, prevents progressive oxidation of the body of the stainless steel below. Amongst the other optional elements, nickel is the most important.

For manufacturing stainless steel, a mixture of steel, stainless steel scrap, chromium (in the form of ferrochrome) and nickel (optional) is charged into an electric arc furnace (EAF) and smelted. Carbon (the original carbon present in the steel plus that getting into it through the ferrochrome) is an important factor in stainless steel. It melts in the EAF, and combines with chromium to form chromium carbide thus robbing the stainless steel of a portion of the chromium added. This problem can be overcome by adding ferrochrome containing very low carbon or by adding ferrochrome containing high carbon with simultaneous decarburization of the molten bath by argon oxygen decarburization (AOD) and vacuum oxygen decarburization (VOD) technologies. The aim is to minimize formation of chromium carbide and maximize the availability of chromium for alloying. Examples of stainless steels are:

<i>Chromium content</i>	<i>Other elements</i>	<i>Properties/Uses</i>
12%	0.3% C	Hard. Used in table knives.
14-18%	0.12%(max) C	Nonhardenable.
14-18%	0.12%(max)C; 0.15%(min) Se	Free machinability.
16-18%	0.95-1.20% C; 0.75%(max) Mo	Fully hardenable.
23-27%	0.2%(max) C	Resistant to scale formation when hot.
18%	18%Ni; 0.07% C; 3.5% Mo; 0.6% Ti; 2.0% Cu.	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (e.g. chemical equipment).
24-26%	19-22%Ni; 0.08% (max) C	Uses requiring resistance to scale and stress at temperatures as high as 1000°C (e.g. staking equipment, furnace parts).
16-18%	6-8%Ni; 0.15%(max) C	Ferritic. Hardenable.
(+) 20%	Low nickel	Mixture of austenite and ferrite (duplex); can be strengthened by addition of nitrogen. Very high performance stainless steel, strong, with high corrosion resistance and very good weldability. Used in appliances, in nuclear stations, in fabrication of large diameter tubes, in coins.
18-20%	8-12%Ni; 0.8%(max) C	Austenitic; superior corrosion resistance.
18-20%	8-12%Ni; 0.03%(max) C	Resists formation of chromium carbide around crystal boundaries.
16-18%	10-14%Ni; 0.08%(max) C; 2-3% Mo	Superior corrosion resistance.

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<i>Chromium content</i>	<i>Other elements</i>	<i>Properties/Uses</i>
17-19%	9-12% Ni; 0.08% (max) C; 5-times carbon- content Ti	Resists formation of chromium carbide around crystal boundaries.
17-19%	9-13% Ni; 0.08% (max) C; 10-times carbon- content Nb	Resists formation of chromium carbide around crystal boundaries.
17%	4% Ni; 3.5% Cu	Martensitic. Used in aircraft industry.
20%	34% Ni; 3.5% Cu; 2.5% Mo	Austenitic; highly resistant to action of sulphuric acid.
21%	0.3% Ti	Nickel-moly free stainless steel. Resistant to corrosion, malleable, low cost.

(3) **Nickel chromium alloys:** These alloys are rich in nickel with chromium and other metals. Nickel and chromium readily dissolve. Such alloys are very highly resistant to corrosion, acids, alkalis and heat. Some of the grades possess good electrical resistivity, and some others are resistant to creep at high temperatures. There are five grades:

- Inconel containing 76% Ni, 15.8% Cr, 7.2% Fe, 0.2% Si, 0.1% Cu and 0.04% C; it is resistant to corrosion at high temperatures. It finds application in engineering goods for use in severely corrosive environment at high temperatures.
- Incoloy containing 32% Ni, 20.5% Cr, 46% Fe, 0.3% Cu and 0.04% C; it resists oxidation, carburization, corrosion and sulphur attack at high temperatures.
- Nimonic containing 58% Ni, 20% Cr, 17% Co, 2.5% Ti, 1.5% Al and 0.13% (max) C; it is creep resistant at temperatures up to 920°C. It is used in gas turbine blades and discs, hot-working tools.
- Nimocast containing 76% Ni, 19% Cr, 0.3% Mn, 0.3% Cu, 0.4% Ti, 0.3% Al, 1.5% Co and 0.1% C; it resists oxidation at temperatures up to 1100°C. It is a casting alloy.
- Nichrome with two sub-grades namely, (i) “*chronin*” containing 80% Ni and 20% Cr; and (ii) “*ferrochronin*” containing 60% Ni, 15% Cr and 25% Fe. Both possess high electrical resistivity and resistance to thermal shocks due to repeated heating and cooling. They are used in heating elements of electric furnaces, toasters, stoves etc. The former is suitable for use at temperatures up to 1150°C and the latter, up to 800°C.

(4) **Other alloy steels:** These can be made by adding some chromite directly to steel furnaces along with ferrosilicon as the reductant or, more commonly, by adding a suitable type of ferrochrome depending on the composition of the alloyed product aimed at. Some important types of products are:

<i>Alloy</i>	<i>Composition</i>	<i>Uses</i>
1% Chromium-molybdenum steel	0.4% C; 0.8% Mn; 0.9% Cr; 0.2% Mo	General purpose bolts, motor axles, crank shafts etc. requiring high tensile strength.
3.5% Nickel-chromium-molybdenum steel	0.3% C; 0.6% Mn; 2.5% Ni; 0.6% Cr; 0.6% Mo	For withstanding severest of mechanical stresses and tempering as in axles and transmission shafts of trucks and tractors.
9% tungsten hot die steel	0.3% C; 2.5% Cr; 9.0% W	Hot forging and punching dies for rivets; bolts; extrusion pads; die-casting dies for aluminium and copper alloys.
High carbon 12% chromium die steel	2.0% C; 12.0% Cr	Uses requiring capacity to resist corrosion and extreme pressure such as plastic-moulding dies, blanking- and press-cold-forming dies, and thread-rolling dies.
Silicon-chromium-tungsten shock resistant steel	0.55% C; 1.0% Cr; 2.0% W; 0.6% Si	Chisels; snap and caulking tools; heading and nail dies; engrossing punches.
18% tungsten general purpose high speed steel	0.75% C; 4.5% Cr; 18.0% W; 1.25% V	Drills; reamers; lathe tools; broaches; milling cutters; punches; dies.
12% cobalt super high speed steel	0.8% C; 4.5% Cr; 21.0% W; 1.25% V; 12.0% Co	Heavy duty machining on high tensile alloy steel; forged products; close-grained cast iron products; railway coach tires.
Kanthal (iron-chromium-aluminium alloy)	75% Fe; 20% Cr; 4.5% Al; 0.5% Co	Can be used in oxidizing atmosphere at high temperatures up to 1350°C as in the case of making elements in high temperature furnaces.
Rustless iron	2-5% Cr	Furnace parts, diesel engine valves.
Nickel-chrome case hardening steel	0.12% C; 0.35% Mn; 3.25% Ni; 0.9% Cr	Used in highly stressed gears of trucks and buses, in heavily loaded shafts, and in plastic moulding dyes.
Nickel-chrome-molybdenum case hardening steel	0.15% C; 0.5% Mn; 4.2% Ni; 1.2% Ni; 0.2% Mo	Used where very high core strength is required, as in transmission gears and plastic moulding dyes.
Nitralloy steels	0.2-0.5% C; 0.35% Si; 0.65% Mn; 1.6% Cr; 1.1% Al; 0.2% Mo; balance nitrided steel	Surface-hardened steel which are machinable.

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<i>Alloy</i>	<i>Composition</i>	<i>Uses</i>
Hadfield steel or austenitic manganese steel with added chromium	C 0.92-1.4%; Mn 12-14%; Cr 1.8-2.2%	High toughness and ductility with high work hardening capability and good abrasion resistance under impact; suitable in rails, earth-moving machinery, mining machinery including rock crushers, grinding mills, dredge buckets, power shovels, bucket teeth and pumps. Addition of Cr enhances resistance to atmospheric corrosion and abrasion.
Titanium vanadium chromium aluminium beta alloy	Ti 73%; V 13%; Cr 11%; Al 3%	Good weldability; high density; thermally stable above 370°C; amenability to cold working. Used in cold-headed bolts.
Stellite	25-30% Cr; 1% (max) Mo; 2-15% W; 0.25-3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co	Used in hard facing materials (e.g. armaments, cutting tools).

(5) **Chromium metal:** Until 1950s, metallic chromium used to be made by the aluminothermic route. It involved smelting of chromic oxide. The grade of the metal was 97% (min) Cr and 1% (Max) Fe. In this method, chromite is first oxidized by air in molten alkali to yield sodium chromate ($\text{Na}_2\text{Cr}_2\text{O}_4$), which is converted to Cr_2O_3 (chrome oxide green) by dissolving it in water. The oxide is then precipitated and reduced by carbon. The metal thus obtained is further reduced and refined by aluminium powder. But the method is costly. Alternatively, the final refining can be done by using silicon as the reductant.

The common method now-a-days, is by electrolysis. This involves dissolution of Cr_2O_3 in sulphuric acid to give an electrolyte. In a process developed by the US Bureau of Mines, the electrolyte was made from high carbon ferrochrome. The purity of electrolytic chromium is 99% (Min) Cr.

There are three types of chromium metal produced:

- (i) High carbon, containing 87% (Min) Cr and 9-11% C.
- (ii) Low carbon, containing 97% (Min) Cr and 0.1% (Max) C.
- (iii) Electrolytic, containing 99.5% Cr and 0.2% C.

(6) **Nonferrous alloys:** Since there is no iron in such alloys, ferrochrome cannot be used as the additive. Instead, chromium metal is used. Stellite, chromin (already described earlier) are example of such alloys.

- (7) **Foundry:** Use of chromite sand as a moulding medium was first practised in the 1950s in South Africa, for producing manganese and steel castings. It is used when a refractory medium is required as in the case of casting of metals with high melting point, where siliceous sand is not suitable. The high fusion temperature, resistance to thermal shocks and chilling effect of chromium are the main criteria. Besides, the brittleness and uneven fracture make it easy to crush it into angular grains. The high fusion temperature and resistance to thermal shocks prevent the casting from damaging the moulding surface. The chilling effect facilitates quick solidification of the casting. Preparation of chromite for this use involves crushing, washing and screening, and freeing it from impurities like silica, talc, serpentine and asbestos by heavy media separation.
- (8) **Chrome-plating:** Chrome-plated surfaces have a bright bluish white finish with a high reflecting power. Also, such surfaces possess a fair degree of electrical resistance. The corrosion resistance, high reflecting power and relatively low electrical conductivity of chromium are the chief criteria. But, chromium plating is not just for imparting a durable and decorative finish to articles of common use, it is also done to resize machine parts by thickening their surfaces, to improve wear resistance of tools, and to line pump rods, engine cylinders and machine gun barrels. Chrome-plating is achieved by precipitation of chromium in an anodizing bath containing chromic acid through electrolysis.
- (9) **Metallization:** Chromium is used to metallize surfaces to make them corrosion-resistant. Metallization is the process in which very small globules of a liquid metal are blown by a spray gun and sprayed on other metal surfaces to improve corrosion or wear resistance. The surface to be sprayed is first roughened by rough-machining or rough-grinding. The molten globules of metal, on being sprayed, immediately solidify and interlock by flattening.

D. Non-metallurgical:

- (1) **Chemicals:** The important chemicals are as follows.
- (a) Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) is the mother chemical from which most of the other chemicals are derived. It is produced directly from chromite. Ground chromite is first roasted with soda ash and lime in the presence of oxygen to separate the impurities iron, alumina and silica of the ore, and to yield a mixture containing sodium chromate, which is extracted by quenching in water and leaching. It is treated with sulphuric acid to finally produce a commercial grade of sodium dichromate. Both the intermediate product sodium chromate and the final product sodium dichromate are important industrial chemicals used for leather-tanning and textile dyeing. It is also used for wood preservation, for manufacture of coloured glass, for organic chemical oxidation, for bleaching of oils, fats and waxes, and as an additive in drilling mud to prolong the life of drill strings.
- (b) Lead chromate (PbCrO_4): In its pure form it supplies the chrome reds. By mixing it with other substances the painters make various yellow pigments. When mixed with Prussian blue, it yields green pigments. It is a natural occurring mineral also – “crocoite” or “red lead”, and the Siberian red lead is prized as a red pigment for oil. But the synthetic chemical, being more easily available and cheaper, is more popular.

- (c) Chromates of zinc and barium (ZnCrO_4 and BaCrO_4): These are extensively used for colouring linoleum, rubber and ceramics.
 - (d) Chromic oxide (Cr_2O_3): One of its products called “chrome green” contains 97–99% of this chemical, and is a green pigment used in paints particularly for outside applications required to withstand severe weather conditions. Other uses include manufacture of linoleum, ceramic glazes, coloured glass, stainless electrode, polishing material and chromium metal.
 - (e) Chromic acid ($\text{CrO}_2(\text{OH})_2$): Its solutions are used in chrome-plating, in anodizing of aluminium and in protection of magnesium-based alloys. It is also used as an oxidizing agent and as a laboratory reagent.
 - (f) Basic chromium sulphate ($\text{CrOHSO}_4 \cdot \text{Na}_2\text{SO}_4$): In leather tanning, it is used to obtain what are called ‘wet blue chrome skins’. Chrome-tanned leather has high wear resistance. This chemical is also used in manufacture of “mineral khaki”.
 - (g) Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): Its main use is in manufacture of safety matches and explosives. Other uses include printing ink, synthetic perfumery, adhesives, engraving and lithography, photography and film processing.
 - (h) Hydrated sodium chromate ($\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$): It is used as an anticorrosive salt in cooling water and chilled brine systems, and as a component in inhibitor formulations.
 - (i) Potash-chrome alum ($\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$): It is used for fixing bath in photography, as a mordant in textile industry, and for leather tanning.
 - (j) Chromium dioxide (CrO_2): It finds use in high quality magnetic audio and video recording tapes.
- (2) **Refractories:** Chromite refractories may be in the form of bricks used for lining furnaces, or mortars used for cementing the pores and joints of the bricks in order to make the linings monolithic and also for repairing furnace linings. The bricks may be based on only chromite or on a mixture of chromite, magnesia, graphite and alumina. They may be chemically bonded, burnt or unburnt, and cased in steel clad which fuses to the brick when in use. Chromite, being cheaper than magnesia, is used to the maximum extent allowed by the nature of use. The ore is used in the form of angular grains, and so its coarse crystalline nature, uneven fracture, brittleness and medium hardness, besides high fusion temperature, resistance to thermal shock, and chemical neutrality (particularly to slags) prove to be the most important criteria.

Earlier, about 90% of the chrome-based refractories produced in India were consumed in steel industry, and the rest 10% in nonferrous metallurgical, glass and cement furnaces. In India, the main problem with pure chrome refractories is its relatively short life span (less than 6 months compared to about 14 months in some other countries) which is now not permitted by the stringent economic parameters of steel manufacturing, and so, this type of refractory brick is becoming obsolete. Instead, now-a-days, the trend is to use less and less of chromite and more and more of other ingredients.

The refractory bricks are prepared from the mixture of grains of the components moulded to shape with a binder (resin, molasses or some chemical) and fired at high temperature. The role of the binder is very crucial. During the glassy phase through which the refractory

passes in the hot furnace, the binding matrix regulates its behaviour more than the aggregate, and prevents penetration of the viscous slag into the pores of the refractory. The firing temperature in India is in the range of 1400–1500°C while that in some other countries is as high as 1800°C. The different types of chromite-containing refractories are as follows.

- (a) *Chrome bricks*: Chrome bricks containing 100% chromite are invariably burnt. They have limited use in ingot soaking pits, re-heating furnaces, copper reverberatory furnaces etc., where heavy duty function is not required.
 - (b) *Chrome-magnesite bricks*: In such bricks containing chromite and dead-burnt magnesite (DBM), chromite predominates. The bricks may be burnt or unburnt. These are used in certain parts electric arc furnace (EAF), open hearth furnace (OHF), glass tank furnace, nonferrous metal smelting furnace etc.
 - (c) *Chemically bonded chrome magnesite bricks*: These are also chrome-magnesite bricks. But in such bricks, a greater part of the chromite is replaced by some chemical bonding material, reducing its content to 18–22%, while that of magnesite remains at 35–48% level. These are not burnt, lest the chemical may get destroyed. These are preferred to ordinary chrome-magnesite bricks in the EAF, OHF and nonferrous metal industry.
 - (d) *Magnesite-chrome bricks*: In these, the ratio of chromite to magnesite should be at least 40:60, and normally a chromite-content of 13–15% and a magnesite-content of 57–76% are maintained by the Indian industries. The bricks may be burnt or unburnt. These are used in EAF, OHF, basic oxygen furnace (BOF), nonferrous metal furnace, rotary cement kiln, glass tank furnace etc.
 - (e) *Chemically bonded magnesite-chrome bricks*: The composition is similar to that of magnesite-chrome bricks, but in this case the bricks are chemically bonded, unburnt and may also be with steel clad. The main uses are in EAF, OHF, nonferrous metal furnace.
 - (f) *Chrome-alumina bricks*: This is one of the latest products which is gaining popularity. In this type of bricks, fine particles of chromite or pure Cr_2O_3 is incorporated in high alumina refractories to the extent of 3.5–5.0% as the binding matrix. The Cr_2O_3 forms solid solution in Al_2O_3 , forming a dense layer at the slag/refractory interface. This results in reduction in slag penetration and in reaction at elevated temperature due to increased viscosity of the glassy phase of the refractory.
 - (g) *Chromium carbide and chromium boride bricks*: These are also used in refractories, but to a much lesser extent than chromite. In India, such bricks are not known to be produced.
- (3) **Human health**: Of the two main forms of chromium, the trivalent chromium is critical for human body, because without it, the hormone insulin does not work; while the hexavalent chromium is poisonous. Both these forms are released during mining and industrial processes, and they enter into air, water and soil. The trivalent chromium gets into human body through soil, food and water and helps metabolism. The air, water and food contaminated with hexavalent chromium released during mining, beneficiation, chrome plating, dyeing, leather tanning and other industrial processes, is carcinogenic.

SPECIFICATIONS OF USE

From the foregoing, it is clear that there are only nine applications for which chromite is directly used. These are:

- (1) Beneficiation
- (2) Agglomeration
- (3) High carbon ferrochrome
- (4) Charge chrome
- (5) Silicochrome
- (6) Low carbon ferrochrome
- (7) Foundry
- (8) Chemical
- (9) Refractory

The discussion on specifications of chromite is, therefore, confined to these.

(1) Beneficiation: Before the advent of beneficiation technology in India i.e., till the early 1990s, generally, the chromite containing less than 30% Cr was not considered suitable for use even for blending purpose. For some of the producers, ore containing even up to 38–42% Cr was uneconomic to use. But the scenario changed in the 1990s. Now, for metallurgical use, beneficiation of ores containing 20% Cr with a view to mainly increasing the percentage of chromium and the Cr/Fe ratio has become common, and ores containing even as low as 14–15 % Cr is beneficiated. For use in chemical and refractory industries, even high grade chromite containing more than 40–45% Cr is beneficiated in order to decrease the silica-content to less than one per cent. The feed grades in other countries are:

Philippines	18–45% Cr
Madagascar	30–37% Cr
South Africa	30–33% Cr
Greece	18–20% Cr
Finland	25–35% Cr
Turkey	18% Cr

For metallurgical and chemical uses, the low grade natural fines are beneficiated, while for refractory manufacturing purpose, even high grade fines and crushed lumpy ore may be beneficiated depending on need. Liberation in Indian ores take place at 150–250 micron size.

(2) Agglomeration: For metallurgical use, both natural fines of appropriate chemical composition and concentrates obtained after beneficiation are agglomerated. The particle size of concentrates, in India, generally varies from 150–250 microns, and this size range suits the designs of the briquetting and the sintered pelletization plants.

(3) High carbon ferrochrome: According to the Bureau of Indian Standards (BIS) specifications of 1998, the chromite to be used for manufacturing high carbon ferrochrome should contain: Cr_2O_3 48%(min); Cr/Fe ratio 2.8:1(min); SiO_2 8%(max); Al_2O_3 13%(max); MgO 16%(max); MgO/ Al_2O_3 ratio 1.2-1.4; CaO. 5% (max); SO_3 0.1%(max); P_2O_5 0.02% (max). The principal constituents are chromium and iron, and the constituents like SiO_2 , Al_2O_3 , S, P, CaO and MgO are considered deleterious. These are discussed as follows.

- (i) *Chromium and iron:* The grade of the ore to be used for manufacturing ferrochrome depends on
- the Cr/Fe ratio in the ferrochrome,
 - the recovery of Cr from the ore, and
 - the recovery of Fe from the ore.

The Cr/Fe ratio in the ferrochrome is dictated by the requirement of the user industry. The last two factors depend on the status of technology at a given point of time and the operational efficiency of the plants. The final recovery of chromium worldwide varies from 75–85% i.e., 80% on an average and that of iron is 100 per cent. Taking the Cr- and Fe-contents of high carbon ferrochrome as 65% and 29%, the Cr/Fe ratio can be worked out thus:

$$(\text{Cr/Fe})_{\text{ore}} = \frac{(\text{Cr/Fe})_{\text{alloy}}}{\frac{\text{Recovery of Cr}}{\text{Recovery of Fe}}} = \frac{65/29}{80/100} = 2.8$$

Once this ratio gets fixed, then the chromium, or for that matter Cr_2O_3 , and also the iron in the ore get specified.

If now, any of the parameters – Cr/Fe ratio in alloy or the recoveries of the metals – changes, then the Cr/Fe ratio in the ore will also change accordingly, and so will the total of all the deleterious constituents making up the balance.

However, depending on the grade of the available ore, higher or lower grades of the product can be made. The Indian industries generally get and use lumpy ore containing around 40–41% Cr_2O_3 and fines containing up to 56% Cr_2O_3 . The fines are briquetted (consequently the grade decreases due to addition of binder). The lower grade ores are blended with higher grade ores in the interest of making the best utilization of the locally available resources.

- (ii) *Al₂O₃ and MgO:* Both Al_2O_3 and MgO are refractory substances. So, they tend to increase the energy requirement for melting the charge, to decrease the fluidity of the slag and also to increase the volume of slag formation. But, if all the raw materials together contain high phosphorus and sulphur, then slag plays an important role inasmuch as it absorbs these elements, and an optimum level of slag formation is desirable. So, both these constituents should be low, but not too low. In the Indian ores used for manufacturing this product, Al_2O_3 is generally within the range 11–14%, and MgO varies up to 15 per cent.
- (iii) *SiO₂ and CaO:* They together form slag and increase the slag volume. Moreover, slag-forming materials are added to the bath in the furnace, and their presence in the ore causes problems in controlling the composition and volume of the slag. While CaO is not a problem in Indian ore, the SiO_2 in the ores used by the industries generally varies up to 8 per cent.
- (iv) *Phosphorus and sulphur:* If, through the ferrochrome, phosphorus and sulphur are carried into the final product i.e., steel, they reduce ductility and make the steel brittle under shocks, and the steel will be liable to crack at the time of rolling (see also chapter on hematite). Hence these impurities are highly objectionable. But it is also practically

impossible to remove them beyond a point, because these elements are not completely absorbed by the slag, and remain distributed in the contact zone between molten metal and slag, and to remove them even partially, addition of extra flux (limestone) becomes necessary, which means increased fuel consumption and decreased productivity. So, phosphorus and sulphur in the chromite meant for ferrochrome production should be as low as possible, but again compromises have to be made due to constraints of local availability, and also the amounts of these elements coming from other raw materials count. The maximum limits of P- and S-contents in the ores actually used by Indian industries vary up to 0.008% and 0.01 per cent respectively.

- (v) *Size*: Fine particles will choke the furnace and obstruct passage of the air blast. Moreover, chromite particles in the lower size range tend to be blown about within the furnace during smelting and lost to the environment or in the slag. So, either natural lumps or agglomerates are specified. It has been actually found that (–) 10 mm size of ore results in decrease in recovery of chromium by up to 5 per cent or even more. As regards natural lumps, the Indian industry accepts sizes ranging from 10–50 mm. The smelter at Kwekwe, Zimbabwe is said to limit the minimum size to 50–63 mm, while the minimum size fed to South African smelters is 1.0–1.5 mm.

(4) Charge chrome: According to the Bureau of Indian Standards (BIS) specifications of 1998, the chromite to be used for manufacturing high carbon ferrochrome should contain: Cr_2O_3 44% (min); Cr/Fe ratio 1.6:1(min); SiO_2 12%(max); Al_2O_3 10%(max); MgO 12%(max); CaO 5%(max); SO_3 0.14%(max); P_2O_5 0.02%(max). The industries in India uses lumpy ores containing 36–48% Cr and fines containing 33–48% Cr, with Cr/Fe ratio generally varying between 1.8 and 2.7 and SiO_2 between 4 and 10 per cent. These grades are optimized by suitable blending.

Charge chrome contains a minimum of 50% Cr, and taking into account the contents of carbon and silica, the corresponding Fe-content works out to 39 per cent. The metal recovery values are same as in case of high carbon ferrochrome. So, by changing the values in the formula, the minimum Cr/Fe ratio in the ore can be calculated thus:

$$(Cr/Fe)_{ore} = \frac{(Cr/Fe)_{alloy}}{\frac{\text{Recovery of Cr}}{\text{Recovery of Fe}}} = \frac{50/39}{80/100} = 1.6$$

Some of the industries in India produces higher grade charge chrome containing 58% Cr, which means that the corresponding Fe is 31 per cent. By using these values, the Cr/Fe ratio works out to 2.34. The principles underlying the specifications with regard to various deleterious constituents are same as in the case of high carbon ferrochrome.

(5) Silicochrome: Since, this is a low-iron product and is also the raw material for manufacturing high carbon ferrochrome, low Fe-content, and consequently high Cr/Fe ratio (implying high Cr-content) in the ore are necessities. According to the Bureau of Indian Standards (BIS) specifications of 1998, the chromite to be used for manufacturing high carbon ferrochrome should contain: Cr_2O_3 48%(min); Cr/Fe ratio 3:1(min); SiO_2 10%(max); Al_2O_3 13%(max); MgO 14%(max); CaO 5% (max); SO_3 0.1%(max); P_2O_5 0.02% (max). The Indian industries use ores containing 48-53% Cr_2O_3 , up to 6% SiO_2 , and with Cr/Fe ratio 3:1. Hard lumpy ores are used. Ranges of sizes are wide, like 6–25 mm, 50–125 mm etc.

(6) Low carbon ferrochrome: According to the Bureau of Indian Standards (BIS) specifications of 1998, the chromite to be used for manufacturing low carbon ferrochrome should contain: Cr_2O_3 48% (min); Cr/Fe ratio 3:1 (min); SiO_2 5% (max); Al_2O_3 13% (max); MgO 14% (max); CaO 5% (max); SO_3 0.1% (max); P_2O_5 0.005% (max). The industries in India uses more or less the same grade of ore. Ore in the form of fines is used. Since, within the furnace there is no air blast (consequently there is no question of any choking to cause obstruction to the blast), nor any reduction involved and the ore has only to melt and combine with molten lime to form a slag, lumpy ore is not necessary.

The average chromium content in the low carbon ferrochrome is 70 per cent. Since the carbon and silica contents are nil or negligible, the entire balance of 30% is constituted by iron. While the recovery of iron is 100 per cent, that of chromium is less in this case than in the case of high carbon ferrochrome or charge chrome. There is no loss of chromium value in making the chromite/lime slag, and so recovery at this stage is 100 per cent. The recovery of chromium in smelting to silicochrome is 80%, and its recovery in the final process of treatment of the slag with silicochrome is 80-85 per cent. Thus the final recovery works out to about 76 per cent. Putting these values in the formula, the Cr/Fe ratio can be worked out thus:

$$(Cr/Fe)_{ore} = \frac{(Cr/Fe)_{alloy}}{\frac{\text{Recovery of Cr}}{\text{Recovery of Fe}}} = \frac{70/30}{76/100} = 3$$

The principles underlying the specifications with regard to various deleterious constituents are same as in the case of high carbon ferrochrome.

(7) Foundry: According to the BIS specification of 1997, the chemical composition of the chromite for use as foundry sand, should be: 44% (min) Cr_2O_3 ; 20% (max) FeO ; 14% (max) Al_2O_3 ; 7% (max) SiO_2 ; 3% (max) CaO ; 14% (max) MgO . But the most important parameter is that the chromite must break in angular grains so as to make a nonporous coating on the surface of the mould. In case of spherical grains, there will be considerable intergranular spaces through which the molten metal may penetrate. If the foundry sand is for casting steel, then iron may not be very strictly objectionable, but for nonferrous metal castings it is. For steel casting, the industries in India specify 44% (min) Cr_2O_3 ; 26% (max) Fe_2O_3 ; 4% (max) SiO_2 ; 0.5% CaO ; 0.5% moisture; and 0.5% LOI. The other deleterious constituents will be liable to enter into reactions with the molten metal. Moisture and the gases forming the LOI will become vapour and get trapped in the casting as bubbles.

(8) Chemicals: Chromite is used for making sodium dichromate which is the mother material for making other chemicals. The process for making sodium dichromate involves roasting with soda ash and lime and separation of the impurities of the ore. Since soda ash is a costly material in India, the specifications are mainly focused on making this roasting as efficient as possible. So, alumina and magnesia are particularly objectionable, because they react and consume soda ash. Also fines are preferred to facilitate complete digestion of chromite by soda ash. Needless to say that chromium should be as high as possible; and consequently iron, which is at the cost of chromium, should be as low as possible. Silica is objectionable because it reacts with the lime to form calcium silicate during roasting, thus consuming a part of it and contaminating the product. CaO in the ore is considered deleterious because lime is added along with soda ash for roasting, and additional lime creates problems in controlling the operations.

According to BIS specification of 1988, the chemical composition of chromite for use in chemical industry is: 44%(min) Cr_2O_3 ; 20%(max) FeO ; 14%(max) Al_2O_3 ; 7%(max) SiO_2 ; 3%(max) CaO ; 14%(max) MgO . But the Indian industries use higher grade ores containing 50–54% Cr_2O_3 , 3.4–3.7 Cr/Fe ratio, 9–11% Al_2O_3 ; 14–15% Fe_2O_3 ; 4–7% SiO_2 .

(9) Refractories: Although, fine grains of (–) 10 mesh or even (–) 65 mesh size ultimately go into refractory brick making, crushed lumpy ore, and not natural fines, are preferred for high quality bricks. There are two reasons for this. Firstly, the natural fines were generally the result of metamorphism accompanied by tectonic dislocations, and there are minute fissures and fractures developed within the individual grains of such ores. When the bricks made out of such ores form the lining in a steel-making furnace, the molten iron oxide enters into the grains of the bricks through the micro-fractures and tend to crystallize. The tremendous force of crystallization results in bursting of the bricks (the phenomenon is known as “*bursting expansion*”). The fine grains obtained by crushing hard and compact ore do not suffer from this problem. Secondly, apart from the size, the shape of the grains is important. Unlike natural fines, the hard compact ore contains well preserved coarse crystals which break with uneven fracture pattern into angular grains. Such angular grains are required for brick-making, because the corners of the grains fuse and bond together forming a strong compact brick.

Alumina is highly refractory, so it is a desirable constituent in the chromite. But FeO and SiO_2 tend to decrease the fusion temperature and resistance to thermal shocks of the bricks, and hence are considered deleterious. CaO is objectionable because it takes away the Al_2O_3 , to form, along with silica, molten aluminosilicate which, when solidified, will break and weaken the brick. Chromite, due to its association with serpentinite, tends to contain serpentine which shows in the assay as MgO . But serpentine is highly deleterious. Its composition is $3MgO.2SiO_2.2H_2O$, the water constituting about 13 per cent. During brick-manufacturing, this water is expelled in the high temperature, and may leave pores within the brick. If some water still remains in the brick lining, its vapour may get entrapped within the steel forming bubbles.

In earlier times, the Indian industries used to specify a minimum limit of Cr_2O_3 at 40%, that of $Cr_2O_3 + Al_2O_3$ at 60% and the maximum limits of FeO , SiO_2 and CaO at 20%, 5% and 1% respectively. Setting no limit for Al_2O_3 , the BIS has classified the chromite refractories into three grades I, II and III. According to the BIS specification of 1999: *with increase in the grade of the refractory the minimum contents of Cr_2O_3 should increase from 48% to 52%, maximum contents of SiO_2 would decrease from 9% to 3%, maximum contents of FeO from 18% to 16%, and the contents of MgO and LOI would remain constant at 15% and 1.5% respectively; the size of the lumps should be in the range (–)150 mm and (+)50 mm.* In some other countries, low grade lumpy chromite containing 30–40% Cr_2O_3 is specified, but that is compensated by high alumina content.

Now-a-days, due to scarcity of low-silica high grade lumpy ore, the Indian industries use a blend of crushed lumpy ore and low-silica high grade natural fines for making ordinary bricks. However, for high quality bricks, they use at least 90% high grade lumps with less than 3% silica with the balance comprising natural fines containing 52%(min) Cr_2O_3 and 4%(max) SiO_2 which is washed to bring down the silica content to less than one per cent. For chrome-alumina bricks, natural fines of chromite containing around 52% Cr_2O_3 with 5.5% silica is considered suitable.

So far as this industry is concerned, there is no limit to deviations from the ideal standard grade of chromite, as there is no limit to the variations in the nature and quality of the end product.

WASTE UTILIZATION

Utilization of wastes on a regular basis is practised in only chemical and refractory industries by way of recycling of wastes. In one of the industries in India manufacturing chromite-based chemicals, recycling of 3–4 tonnes of waste material comprising a mixture of chromite, iron, alumina, silica, calcium oxide etc. per tonne of sodium dichromate produced, has been reported. In the Indian refractory industries, the scarcity of low-silica lumpy ore has forced the producers to substitute it by waste bricks to the extent of up to 25 per cent.

SUBSTITUTION

So far as metallurgical uses are concerned, chromite has no substitute, except in foundry. Other non-siliceous moulding media like zircon and olivine sands, which possess comparable refractory properties, may substitute it. Although zircon sand is more refractory, the chilling ability and lower cost of chromite make it preferable in production of many types of casting. However, in certain cases chromite is partially substituted by zircon and a mixture of the two is used.

Amongst the nonmetallurgical products, chromite refractory bricks are substituted by the iron and steel industry in India by various superior products like magnesite-carbon bricks in keeping with the changing technologies requiring higher and higher performance levels. Besides, increasingly more stringent cost control measures demand longer life refractories.

The reluctance of Indian glass industries to use chromite-based bricks is for a different reason. The carcinogenic hexavalent chromium present in the major chromite deposits of India tends to get into the glass through the refractory bricks, and this makes their products unacceptable to the users.

ILMENITE AND TITANIUM

Although, ilmenite is the only commercial source of titanium metal in the world, in India it has traditionally been considered as an industrial mineral, its usage here being practically limited to titanium-based chemicals and pigments; but nevertheless some quantities of ferro-titanium is also manufactured. Since the beginning of the 21st century, however, its potential as an ore of titanium metal is increasingly being recognized in India too, and projects for recovery of titanium is being planned. Hence in this book, it has been grouped as a metallic mineral.

Ilmenite is a titanate of iron having composition $\text{FeO} \cdot \text{TiO}_2$. Ilmenite crystals were first studied in Ilmen Mountains in Russia, from which the name ilmenite has been derived. It occurs associated with magnetite in basic igneous rocks like gabbros and diorites. Such primary deposits are mined in some places in Adirondack region, New York, USA. But, worldwide, the most important commercial resources of ilmenite occur in the black heavy mineral sands – both inland river placer and beach placer. In India, the beach placer deposits of Kerala, TamilNadu, Andhra Pradesh and Orissa constitute the only deposits of economic significance.

Ilmenite theoretically contains 31.6% titanium (equivalent to 52.67% TiO_2), 36.8% iron and balance oxygen. Sometimes, magnesium may replace part of iron. An alteration product of ilmenite called leucoxene contains higher percentage (60% or more) of TiO_2 . But, in nature, primary ilmenite occurs along with other minerals as impurities, and the TiO_2 -content is much lower. But almost pure ilmenite (or leucoxene) can be separated from the placer sand.

Titanium is the 9th most abundant element in the earth's crust, but it does not occur in native state. Dana has recorded 46 titanium minerals, out of which the relatively more important ones are ilmenite, rutile (TiO_2), anatase (a dimorph of rutile with the same chemical composition) and titanite (CaTiSiO_5). Titanium is the heaviest of the trio of light metals – aluminium, magnesium and titanium.

HISTORY

Considering the long history of metal usage, all the three light metals are very recent, being 19th century metals, and amongst them, titanium is the most recent addition to the list of metals. Although, it was discovered in 1791 by an English clergyman and amateur chemist William Gregor who separated it from the black sand of Cornwall – perhaps not attaching any significance to the work, the credit of first conscious scientific processing to isolate it goes to J.J. Berzelius, who did it in 1835. But as the processing was limited to only a small sample and as it proved to be a very difficult metal

to isolate, there was no interest shown by anybody till 1906, when M.A. Hunter isolated enough metal for serious study. Eventually, Wilhelm Kroll decided to explore its potentiality as a substitute of beryllium in copper-beryllium alloy in 1928, and succeeded in developing a commercial process for its production during the period 1932-37. This process became known as “*Kroll process*”, and was further improved by the US Bureau of Mines (USBM), in the 1940s, leading to first commercial production of titanium metal sponge in 1949. Although in that year the quantity was just over 2 tonnes, in 1957 it reached the level of about 17800 tonnes.

Ilmenite concentrate was however being produced in many countries since 1918 i.e., well before the technology for titanium metal was in place – mainly for the industrial value of TiO_2 . Although, in India, the industrial processing of ilmenite did not start till 1951, its mining started in India in 1912, and she was the leading producer of ilmenite during 1930s and 1940s. But during the World War-II (1940-45), its supply to USA from India by the sea route got cut off, and the deposits of USA started being opened up. By the end of 1948, USA became the top producer in the world.

The history of production of ilmenite in India can be traced back thus. The monazite sand deposit of Kerala in India was discovered in 1909. Coir workers of that region used to rub their hands in sand to get a grip of the coir. Some sand used to stick to the wet coir. Eventually, some sand found its way to Germany along with the exported coir. One day, in 1909, C.W. Schomberg, a chemist, by chance, stumbled upon this glistening sand. He could identify that the sand contained monazite, an important material for gas light mantle. He came to India and located the deposits. He established a separation plant in 1911, and in that year exploitation also commenced. Now the monazite sand was very rich in a number of heavy minerals one of which was ilmenite. So, in the plant, ilmenite concentrate also started being separated. The British took over it during World War-I (1914–18). After independence (1947), in 1950, the Government of India created a new undertaking, namely the Indian Rare Earths Ltd. (IREL) for mining and processing of the heavy mineral sand resources of India. The production history of ilmenite in India is shown below:

<i>Year</i>	<i>Production</i>
1912	Approximately 405 tonnes
1930	Approximately 30000 tonnes
1935	Approximately 130000 tonnes
1940	Approximately 260000 tonnes
1945	Approximately 175000 tonnes
1948	Approximately 310000 tonnes
1950	Approximately 215000 tonnes
1965	Approximately 30000 tonnes
April, 2000–March, 2001	Approximately 428000 tonnes

The drastic fall in production after independence was due to opening up of mines in USA, transforming it to a self-sufficient country from one that was largely dependent on supplies from India. But gradually India’s ilmenite industry started recovering.

The world production of ilmenite which was in the region of 350000 tonnes in 1933, increased to 365000 tonnes in 1938, and then to about 725000 tonnes in 1948 and almost one million tonnes in 1953. By the year 2000, the annual world production reached 9.6 million tonnes.

RECOVERY

From ilmenite, both TiO_2 (for various non-metallurgical uses) and titanium metal is recovered. This TiO_2 (also called “*synthetic rutile*”) may be converted to metal. Kroll process (also known as “chloride process”) is the universally accepted standard process for recovering titanium metal from ilmenite directly or from TiO_2 . This employs the chlorination route, which, till date, is the most environment-friendly. But if TiO_2 is to be produced from ilmenite, then, a process called “sulphate process” is used, because the chloride process, for this purpose, requires high TiO_2 -content (over 90%) in the feedstock and is not suited to ilmenite as such. To make the ilmenite amenable to chloride process for production of TiO_2 , it will be necessary, therefore, to upgrade the ore first. A process has been developed in Brazil, in the early 1980s, for upgrading primary ilmenite ore containing as low as 25% TiO_2 to (+) 90% grade. But this involves additional cost.

In the sulphate process, finely ground ilmenite is digested in concentrated sulphuric acid (98% concentration) to yield a liquor containing the sulphates of titanium and iron along with impurities containing Al, Si, P and Mg. When this liquor is progressively diluted with water in a controlled manner, at first, while the titanium and iron sulphates remain in solution, those other impurities precipitate, which are removed by filtration. Further dilution makes the sulphates also to precipitate, which are recovered by filtration. The mixture of sulphates is then dissolved in water at elevated temperature with seeds of pure TiO_2 crystals (either rutile or its dimorph anatase) added. As a result, titanium hydrate crystallizes and precipitates, while the iron sulphate remains in solution, which is decanted off. The titanium hydrate is washed. But this titanium hydrate still contains some titanium sulphate as impurity, and it is then calcined at 600–650°C, as a result of which both the water and SO_2 get removed leaving solid TiO_2 . If the seeds are of rutile, then the TiO_2 produced is of purer grade than if anatase seeds are used. This process suffers from the disadvantage that as much as 4 tonnes of $\text{Fe}(\text{SO}_4)_2$ for every tonne of TiO_2 recovered, is generated as a solid waste, and that the sulphuric acid being not recoverable has to be discharged. On both these counts, not only environmental damage is caused, but also consumption of acid becomes high.

In the chloride process, ilmenite or crude TiO_2 is chlorinated to produce FeCl_2 and titanium tetrachloride (TiCl_4), which being soluble in water, can be separated by filtration. For producing high purity TiO_2 , this tetrachloride is hydrolyzed with seeds of pure TiO_2 to precipitate titanium hydroxide, and finally to the product TiO_2 in the same way as in sulphate process described above. For the purpose of producing titanium metal, however, the TiCl_4 is treated with red-hot magnesium metal under an inert gas blanket (the inert gas is necessary because liquid titanium tends to absorb oxygen and nitrogen very rapidly). The resultant products are commercially pure spongy titanium metal and MgCl_2 . The MgCl_2 is drained out and electrolyzed to recover both chlorine and magnesium for re-use. However, part of the chlorine is lost in FeCl_2 (for 1 tonne of TiO_2 , 1.2 tonnes of FeCl_2 is generated). The titanium sponge mixed with titanium scrap is melted into a primary ingot in water-cooled copper crucibles. If titanium alloys are to be made, then the alloying elements are added at this stage. The primary ingot is re-melted in electric arc furnace to get the final ingot, which is suitable for forging, rolling, drawing etc. to make the desired products. Since part of the hazardous chlorine is recaptured and recycled and the solid waste comprising FeCl_2 is only 1.2 tonnes per tonne of TiO_2 , this process is more environment-friendly than the sulphate process.

Smelting reduction (SR) technologies like “direct AC arc smelting” and “direct DC plasma smelting” for extracting titanium directly from ilmenite are also practised. Plants based on the former are in operation in Canada and South Africa, while those based on the latter are in operation in South Africa.

In India, ilmenite is recovered from beach placer deposits containing 10–25% heavy minerals comprising ilmenite, rutile, zircon, monazite, garnet, sillimanite and leucosene. For recovering ilmenite, beach sand is first washed to 50% heavy mineral concentration. This concentrate is subjected to spiral separation in a series of plants to get 90% concentration. Finally, this concentrate is dried and separated into ilmenite and other individual minerals utilizing differences in physical properties of the minerals, such as electrical conductivity, magnetic susceptibility, specific gravity, grain size etc. As in 2005, the ilmenite, in India, is processed for TiO_2 pigment production by the sulphate route. According to a report (May, 2005) of researches conducted in Regional Research Laboratory, Bhubaneswar, results of pilot plant scale trials for direct smelting of ilmenite in extended arc plasma reactor using pre-reduced ilmenite, although highly energy-intensive, was encouraging. It has been claimed that the process yielded 80–85% TiO_2 grade slag, which on acid leaching yielded TiO_2 (synthetic rutile) of 93–94% grade.

CRITERIA OF USE

The criteria for using ilmenite as the feedstock for recovery of titanium metal and oxide are its chemical composition, and abundant availability in nature and consequent low cost. The criteria for various uses of titanium metal and oxide are as follows:

A. Titanium metal

- (1) *Strength and specific gravity*: Titanium has specific gravity of 4.5. It is 60% heavier than aluminium and 56% lighter than alloy steels, but is stronger than aluminium. Its strength to weight ratio at ordinary temperature exceeds that of both of them.
- (2) *Colour*: It is silver white in colour – between silver and stainless steel.
- (3) *Corrosion resistance*: It has excellent resistance to corrosion in oxidizing media, and to action of atmosphere and salt water.
- (4) *Thermal properties*: It melts at 1690°C and boils at 3535°C . Its thermal conductivity is low, and coefficient of expansion is 8.5×10^{-6} . It does not burn till 538°C , but above this temperature it burns in air rapidly.
- (5) *Electrical and magnetic properties*: It is low in electrical conductivity (3.1% of standard copper i.e., International Annealed Copper Standard or IACS) and is paramagnetic. But some of its compounds (e.g., barium and barium-strontium titanates) exhibit excellent electrical conductivity and piezoelectric effects (piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice-versa).
- (6) *Stability*: It has remarkable stability of properties over a wide range of temperature from (-160°C) to $(+538^\circ\text{C})$.
- (7) *Chemical affinity*: Above 538°C , it absorbs oxygen and nitrogen to form oxide and nitride respectively. At high temperature, its stronger affinity for oxygen and halogens than for hydrogen enables it to absorb oxygen and chlorine from water vapour and hydrochloric acid respectively and release hydrogen. Titanium also possesses strong affinity for carbon and forms its carbide (TiC) at high temperature. Its compounds with barium and strontium can also be formed at high temperature. Some organic compounds are also made.

B. Titanium dioxide

- (1) *Colour and brightness*: Titanium dioxide is a bright white substance with refractive index of 2.7 (cf. 1.0 of vacuum and 2.42 of diamond) and high dispersion (dispersion is the rate

of change of refractive index with change in wavelength of the incident light). The high refractive index combined with high dispersion gives it an adamantine lustre and a brilliant appearance.

- (2) *Lightness*: Its specific gravity is low, being around 4.
- (3) *Opacity and light reflectivity*: It has the highest white hiding power amongst all the known white pigments. In fine particle size, it reflects both visible and ultraviolet light rays. The thumb rule is that the particle size should be half of the wave length of the light ray to be reflected. The wave length of the violet light is 0.4–0.5 microns, which is the shortest for the visible light rays. So, particle size of less than 0.2 microns will reflect and scatter ultraviolet light also.
- (4) *Toxicity*: TiO_2 is nontoxic.
- (5) *Hardness*: It is extremely hard.
- (6) *Refractoriness*: It is highly refractory and can withstand up to 1800°C temperature (a refractory material is defined as one resistant to heat and having a melting temperature of not less than 1580°C).
- (7) *Electrical property*: It is an excellent conductor of electricity with an unusually high dielectric constant of 100 (dielectric constant is the ratio of the capacitance of a specific sample of the material between two plates and a vacuum between the same plates; the value for air, one of the poor conductors of electricity, is 1).
- (8) *Resistance to chemical*: It has a strong ability to resist attacks by acids.
- (9) *Weatherability*: It suffers from the disadvantage that over a long duration of time, it tends to yellow.
- (10) *Catalytic action*: Titanium dioxide in the presence of ultraviolet light acts as a catalyst to facilitate oxidation of a wide range of organic materials.

USES

A. Metal-based uses

- (1) *Titanium metal*: The high strength to weight ratio, resistance to corrosion by sea water and acids, high melting point, burning at a fairly high temperature (which allow an operational temperature up to 500°C) and stability over a wide range of temperature are the key properties. In spite of its superior properties, the only limiting factor is its high cost compared to other common metals. It is therefore used in high value and very strategically important products. The largest military market of titanium metal was initially in aircraft and shipping industries. It makes up 39% by weight of the F-22 military aircraft of USA. Later on, civilian uses in chemical equipment became added. Titanium of 99% and above purity is used in sheet, strip or plate form for making (a) firewalls, bulkheads, compressor cases of aircraft piping, (b) valves and tanks used in chemical industry, (c) salt water valve seals, disc trims, tubing for condenser systems etc. in submarine diesel engines.
- (2) *Alloys*: Despite the superior properties of titanium, its high costs of production and fabrication preclude its wide use in pure form. In fact, it is more used in alloy form in all the uses mentioned above, but which are not strategically very critical. Its uses in alloy form now extend to surgical instruments, orthopedic appliances, light weight non-

corroding golf clubs and tennis rackets, textile machinery etc. But the principal sponsor of titanium research and development continues to be the aerospace industry – particularly some components of turbojet engines. Various components like heat exchangers, pumps and turbines of nuclear power plant reactors constitute another important sector for use of titanium alloys. So far as the automotive industry is concerned, its use is presently limited to the valve train components of high-cost and high-performance racing cars. It has been estimated that installation of a titanium alloy valve train effects 2–4% saving in fuel consumption. The important alloys are:

<i>Alloy</i>	<i>Composition</i>	<i>Functions and uses</i>
(i) 18/8 stabilized austenitic corrosion resistant stainless steel.	0.07% C; 10.0% Ni; 18% Cr; 0.5% Ti.	Suitable for equipment requiring welding without subsequent heat treatment such as hospital equipments, stainless steel sinks.
(ii) 18/18 austenitic corrosion resistant stainless steel.	0.07% C; 18.0% Ni; 18% Cr; 3.5% Mo; 0.6% Ti; 2.0% Cu.	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (e.g., chemical equipment).
(iii) Ferro-titanium (Fe-Ti).	Ti 25–40%.	Alloying addition for producing micro-alloys with some special properties; for welding electrodes, hard facing and de-oxidizing in powder form.
(iv) Electric ferro-titanium (Fe-Ti).	Ti 65–70%.	Alloying addition for producing micro-alloys with some special properties.
(v) Ferro-titanium-aluminium powder (Fe-Ti-Al).	Ti 40%; Al 10%.	For welding electrodes, hard facing and de-oxidizing in powder form.
(vi) Silicon carbide fibre reinforced Titanium-aluminium alloy.	Mainly Ti and Al.	Combines ductility of aluminium with high temperature strength of titanium; suitable for use in spacecrafts.
(vii) Titanium palladium alloy.	Ti 99%; Pd 1%.	Addition of small amounts of palladium improves resistance to non-oxidizing acids. Used in chemical industry.
(viii) Titanium aluminium tin alpha alloy.	Ti 91–94%; Al 4–6%; Sn 2–3%.	Used in aircraft tailpipe assemblies, sheet components, gas turbine compressor rings, missile fuel tanks, where weldability and moderate strength at temperature below 500°C are required.
(ix) Titanium iron chromium molybdenum alpha-beta alloy.	Ti 94%; Fe, Cr and Mo each 2%.	High strength at room or moderately high temperature, but poor weldability.

Contd.....

<i>Alloy</i>	<i>Composition</i>	<i>Functions and uses</i>
(x) Titanium aluminium manganese alpha-beta alloy.	Ti 92%; Al and Mn each 4%.	Poor weldability as above, but addition of aluminium gives high strength at higher temperature.
(xi) Titanium aluminium vanadium alpha-beta alloy.	Ti 90%; Al 6%; V 4%.	Poor weldability as above, but high strength at high temperature. Used in sheet and forgings for airframe parts, and in gas turbine compressor blades.
(xii) Titanium aluminium molybdenum alpha-beta alloy.	Ti 89%; Al 7%; Mo 4%.	Poor weldability as above, but higher strength at high temperature; shallow hardening.
(xiii) Titanium vanadium chromium aluminium beta alloy.	Ti 73%; V 13%; Cr 11%; Al 3%.	Better weldability than the alpha-beta alloys; high density; thermally stable above 370°C; amenability to cold working. Used in cold-headed bolts.
(xiv) Titanium aluminium molybdenum tin silicon alloy.	Ti 87.5%; Al, Mo and Sn each 4%; Si 0.5%.	High strength alloy, used for highly stressed structural components in aircraft and structural engineering.
(xv) Nitinol.	Ni and Ti.	Used to hold broken bones in position for setting; it is preferable to stainless steel which is not resilient enough to yield sustained pressure. When heated by body-heat, nitinol rods expand, but comes back to original position thus maintaining sustained compressive effect.
(xvi) Uranium-titanium alloy.	—	—
(xvii) Thorium-titanium alloy.	—	—
(xviii) Nickel-moly-free stainless steel.	Ti 0.3% ; Cr 21%.	Resistant to corrosion, malleable, low cost.
(xix) Nimocast.	Ni 76%; Cr 19%; Ti 0.4%; Al 0.3%; Co 1.5%; Mn 0.3%; Cu 0.3%; C 0.1%.	Resistant to oxidation at temperatures up to 1100°C casting alloy.
(xx) Nimonic.	Ni 58%; Cr 20%; Co 17%; Ti 2.5%; Al 1.5%; C 0.13% (max).	Creep resistant at temperatures up to 920°C used in gas turbine blades and discs, hot-working tools.

- (3) *Manufacturing of stainless steel, steel, ferrous and nonferrous alloys:* Titanium serves as a carbon- and nitrogen-stabilizing element in stainless steel. One of the methods of decarburization of stainless steel requires addition of titanium, which, having greater affinity for carbon than chromium, combines with the carbon to form stable carbide. Above 538°C, Titanium absorbs nitrogen to form nitride. At high temperature, its strong affinity for oxygen was taken advantage of, during the initial period of growth of titanium industry, in Bessemer process of steel smelting by adding it in the form of ferro-carbon-titanium alloy. There are, however, cheaper substitutes for this application now. Titanium in the form of ferro-titanium is also added during manufacturing of steel, alloys of nickel, cobalt and aluminium, and permanent magnets made of these alloys, because of its gas-removing, grain-refining, age-hardening and strengthening properties.
- (4) *Rocket fuel:* Due to its fast-burning property, titanium powder had been considered to have potentiality for use as a solid rocket fuel. But, later on aluminium and other substances were found to be more suited to this application.
- (5) *Titanium carbide (TiC):* The strong affinity of titanium for carbon enables it to form its carbide (TiC) at high temperature. This carbide is an extremely hard substance, and, earlier, used in some fused or sintered alloys and in abrasive stones for use in tips of cutting tools and abrasive wheels. Now-a-days tungsten carbide is used in most of these applications. It is also incorporated in tungsten carbide for these uses.
- (6) *Transistor:* According to a report (September 2005), world's tiniest transistor made of Y-shaped carbon nanotubes have been created by a group of scientists of University of California. Nanotubes are rolled up sheets of carbon atoms and are more than thousand times thinner than human hair. This research is based on an earlier research of another group of scientists of Jawaharlal Nehru Centre, Bangalore, who used titanium-iron catalyst to grow straight nanotubes of carbon into Y-shaped ones.
- (7) *Metal matrix composites:* A composite material is a materials system composed of a mixture of two or more materials deliberately combined to form heterogeneous structures with desired or intended properties. In composites, at least one of the constituents serves principally to strengthen or reinforce the composite, while another constituent, called the matrix, serves to confine the reinforcing constituent(s) and provides a means to distribute any applied stress. In metal matrix composites (MMCs), a metal serves as the matrix, while the reinforcing constituent can be a metal, a non-metal, an alloy or a compound. So far as titanium-bearing MMCs are concerned, SiC-fibre-reinforced Ti and SiC-fibre-reinforced TiAl have been developed for aerospace applications.
- (8) *Permanent magnet:* Permanent or hard magnets, once magnetized, retain their magnetic field indefinitely even after the magnetizing field is withdrawn. In "alnico" (an alloy of aluminium (8%), nickel (14%), cobalt (25%) and iron (50%)), which is a permanent magnet with magnetic field strength 1500 gauss i.e., 3000 times the earth's magnetic field, and curie point (i.e., the temperature above which a substance loses its magnetism) highest amongst all magnetic materials – 800°C, titanium is added to increase the coercive force (i.e., the demagnetizing force required to reduce magnetic flux density of a magnet to zero). Such magnets are used in generators, motors, communication/acoustic equipment etc.

B. Titanium dioxide (Synthetic rutile)

- (1) *Paint:* White colour, lightness, adamantine luster, brilliant appearance, excellent hiding power, high reflectivity and scattering ability for both visible and ultraviolet light, non-toxicity, hardness, refractoriness and strong ability to resist attacks by acids make TiO_2 an excellent high-performing pigment that is used in white paint after mixing with some suitable media, and by far the bulk of the consumption of all ilmenite is in this industry. Due to lightness, finely ground TiO_2 powder (particle size less than 0.2 microns) is capable of remaining evenly distributed and in suspension in the medium. Also, at this particle size, the powder scatters both visible and ultraviolet light. This increases its value as a pigment. It can also be mixed with other chemicals to yield coloured pigments. For this purpose, even the coloured impurities present in the ore can be taken advantage of. However, it tends to yellow over a long duration of time, and to increase durability, it is used in combination with some filler (e.g., 5–20% of ZnO_2).
- (2) *Enamels and glazes:* TiO_2 is used as an opacifying agent in enamels mainly due to its lustre, hiding power, hardness and resistance to acids. Titanium dioxide enamel finds application on steel and cast iron goods like stoves, refrigerators etc. It is also used (to the extent of 8–12%) to impart pleasing glazes on porcelain, sanitary ware etc., as well as in ivory finish of artificial teeth. It is also used in lacquers.
- (3) *Paper, rubber, textile fabric, floor covering:* Here, the use of TiO_2 is as a coating material on account of its white colour, lightness, adamantine luster, brilliant appearance, excellent hiding power and strong ability to resist attacks by acids.
- (4) *Skin ointment:* Ability of finely ground TiO_2 to scatter ultraviolet light and its non-toxicity are the main criteria for its use in dermatological preparations for protection against sun, particularly in tropical regions.
- (5) *Hydrogen production:* According to some Australian scientists, sunlight can be harvested to generate hydrogen from water with the help of titanium dioxide. For this purpose, a rod made of TiO_2 and another made of platinum are immersed in a solution containing water and a little caustic soda, and the two rods are interconnected at the top end. Then ultraviolet light is allowed to fall on the TiO_2 -rod. An electrolysis-like effect is produced, splitting the water into hydrogen and oxygen ions, the former going towards the platinum rod and the latter towards the TiO_2 -rod. The effect becomes more pronounced if the TiO_2 is replaced by strontium titanate.
- (6) *Self-cleaning fabric:* Titanium dioxide in the presence of ultraviolet light acts as a catalyst to facilitate oxidation of a wide range of organic materials. This property has been made use of by a group of researchers from Hong Kong Polytechnic University in laying the foundation of making “self-cleaning fabrics”. The key to the breakthrough lay in powdering titanium dioxide to extremely small particles of 20 nanometres size (2500 times smaller than the width of a human hair), and then developing anatase crystal structure (tetragonal titanium dioxide crystals in octahedral habit) in these tiny particles. Such nanoparticles act as catalysts that help break down, in presence of sunlight, carbon-based molecules of dirt, grease etc. In the process developed, a cotton fabric is dipped into a liquid slurry made of these particles for just half a minute, removed, padded dry, and then heated to 97°C for 15 minutes.

- (7) *Chemicals:* Titanium tetrachloride (TiCl_4) – a straw-coloured liquid, was used as smoke screen in military operations during World War-II. It has also been used for sky-writing for advertisement or other purposes. Further, it has a strong affinity for sulphur and can absorb H_2S gas to yield TiS_2 and release hydrogen. A titanyl chloride antimony trichloride complex, which was found to be effective as a fire-retardant, has been applied to some types of cellulose fabric. The alkyl titanates derived from the reaction between titanium tetrachloride and alcohols were found to be good waterproofing agents and have been used as water repellent finish to paper, wool, rayon, nylon, silk, wood etc. both titanous chloride and sulphate possess strong iron-removing and colour-reducing properties, and are used for de-staining paper, wool, textile prints, leather, sugar and silica sand that is meant for use in manufacture of optical glass.
- (8) *TiALON:* It is the acronym for titanium, aluminium, oxygen and nitrogen which are combined into a composite material called titanium-aluminium oxy-nitride. This ceramic material having unique electrical properties was developed by the US Bureau of Mines during the late 1980s and early 1990s. This TiALON can be either a conductor or a semiconductor depending on the ratio between the conducting and non-conducting phases. Later on, its modified version has been developed which is a light-weight, tough, corrosion-resistant, insulating ceramic material capable of being applied to a surface by vapour deposition to form an extremely thin uniform coating. It is used in a more advanced form of “*electrode boring*” called “*electrochemical boring*”. These are techniques of making very fine bores (diameter may be as small as 0.004 mm). In conventional electrode boring, a fine platinum wire electrode is inserted within a glass tube, and positive and negative electrical charges from a DC source are applied to the object to be bored and to the electrode tube respectively. Due to flow of electrons, molecules of the object are eroded at the point of its contact with the platinum wire. In electrochemical boring, an electrically conductive thin metal tube containing an electrolyte is used in place of the platinum-glass electrode. Here, role of TiALON is to provide a very thin insulating coating on the metal tube with a view to preventing electrochemical corrosion of the object around the contact point.
- (9) *Ceramic titanates:* These have been finding increasing use in electronic industry. These are characterized by very high dielectric constant (making them excellent conductors of electricity), excellent piezoelectric effect and pyroelectric properties (piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice versa; pyroelectric materials converts heat energy into electric impulses). Some of the titanates are characterized by development of positive temperature coefficient of resistivity (or PTC i.e., the resistivity increases with increase in temperature, and the increase is very large at Curie temperature which is the temperature at which a substance loses its magnetism).
- Titanates are used for manufacturing dielectric ceramics, piezoceramics, pyroelectric sensors and PTC resistors. Dielectric ceramics include ceramic capacitors in disc, tubular and multiplayer shapes. Piezoceramic devices comprise all kinds of electrochemical transducers, high voltage generators, electromechanical resistors, filters in telecommunication and sensing devices in information technology. Pyroelectric properties

provide a basis for uses in infrared detection and thermal imaging. Application of PTC resistors include semiconductors used in current regulators, self-regulating heaters, overheat protectors and demagnetizers in colour television receivers.

The electrical properties of titanate ceramics depend on the porosity and the ceramic microstructure. These are prepared by special forming (such as casting and pressing) and sintering techniques.

Examples of dielectric ceramics are barium titanate (BaTiO_3) and solid solution of barium and strontium titanate $[(\text{Ba,Sr})\text{TiO}_3]$; those of piezoceramics are BaTiO_3 and solid solution of lead titanate and lead zirconate $[\text{Pb}(\text{Ti,Zr})\text{O}_3$ or PZT]; those of pyroelectric ceramics are solid solution series lead-lanthanum-zirconate-titanate (PLZT); and those of PTC resistors are also BaTiO_3 but made semiconductive by substituting lanthanum or neodymium for barium ions. These properties make them suitable for use in television set capacitors, microphones, phonograph pickups, high frequency sound generators and radiators for generation of ultrasonic energy.

Transparent PLZT ceramics are also manufactured. These are used in goggles for thermal and flash protection, in linear electro-optic modulators for voltage sensors, and in electro-optic light gate arrays for optical memories.

- (10) *Synthetic diamond*: Strontium titanate and synthetic rutile (TiO_2) have emerged as a synthetic substitute for natural industrial diamond for high-tech uses.

SPECIFICATIONS OF USE

1. Ilmenite for titanium dioxide pigment: In ilmenite ore, iron oxide constitutes the bulk impurity which along with other gangue minerals have to be removed. When the ore is processed for recovering titanium metal, these impurities get removed one by one, and the metal product is pure enough for its current uses. But when the ore is processed for manufacturing TiO_2 , which is mostly valued for its pigment qualities, even small amounts of deleterious constituents are objectionable. Examples are:

- (i) Colouring substances like iron oxide, chromium oxide, manganese oxide, rare earth elements and niobium compounds.
- (ii) Hard substances like niobium compounds (Niobium is as hard as wrought iron), vanadium and alumina, which will increase the cost of grinding to very fine particle size required (preferably less than 0.2 microns).
- (iii) Substances like niobium compounds that increase heat transfer rate of the pigment.
- (iv) Heavy substances like iron oxides, niobium compounds, manganese oxides etc. that tend to increase the specific gravity of the TiO_2 and decrease its ability to remain in finely dispersed state in the medium.
- (v) Substances like CaO and MgO that act like fluxes and decrease refractoriness.

As regards specifications, a report of researches in Brazil indicated in 1984 that, for manufacturing white pigment by chloride process, natural ilmenite should be beneficiated so as to contain 91% (min) TiO_2 , 2.0% (max) Fe_2O_3 , 0.4% (max) CaO, 0.3% (max) MgO, 2.0% (max) Al_2O_3 , 3.8% (max) Mn and V, 0.4% (max) Rare Earth elements, 1.03% (max) Nb_2O_5 , and 2.0% (max) P_2O_5 . For beneficiation to this grade, the ilmenite used contained 25% TiO_2 .

2. Titanium metal: Titanium metal is a developing industry. The present technology is not enough to yield 100% pure metal. The commercially pure product contains at least 0.25% of carbon, oxygen and nitrogen in alloy state. However, for its present limited uses, up to 1.0% of these impurities is considered tolerable.

SUBSTITUTION

Titanium is a relatively new metal. Its processing is still very cost-intensive, and its potentialities are not yet fully realized. It itself has been substituting some older metals like steel, aluminium etc.—mostly in the form of alloys. So, question of substituting titanium is premature.

However, for recovery of TiO_2 and titanium metal, there are three important alternatives to ilmenite, namely natural rutile, high-titanium slag generated from smelting of titaniferous hematite ore as those of Canada and USA, and leucoxene. As for rutile, it is scarce and costlier compared to ilmenite, and may, therefore, be of economic significance only if sufficient natural ilmenite is not available at economic distance. Titanium slag is a man-made feedstock and contains up to 87% TiO_2 (beneficial to 95% grade), and its price per tonne of titanium content is in between that of natural ilmenite and rutile. For extracting titanium from slag, smelting reduction processes are employed. Leucoxene, which is an alteration product derived from ilmenite, can, however, be used interchangeably with ilmenite.

IRON ORE : HEMATITE

HEMATITE

Hematite is an oxide of iron having composition Fe_2O_3 . Pure hematite, also called “*red ore*” (in fact, the name hematite comes from the word “hemo” meaning blood), contains 70% of Fe. Almost pure hematite occurs on the edge of Cockatoo island in Western Australia. But generally it contains various other constituents namely SiO_2 , Al_2O_3 , P, S, TiO_2 , Zn, Cu, As, Sn, Cr and Ni. Out of these, the first four are common in Indian hematite. In nature, its structure is varied starting from compact specular and columnar to foliated (micaceous hematite). When mixed with clay or sand, it is called *argillaceous hematite* or *clay iron stone*. The coarse-grained variety with brilliant metallurgical luster is known as “*specular iron ore*”.

Hematite is the most widely distributed and mined iron ore. Mining is generally by open cast method. The only exceptions are a few underground mines in USA and the Hiparsa mine in Argentina, which was mined by underground method till 1993, and plans were afoot in 2004 to revive it. Kryvy Rih of Ukraine and Carajas of Brazil are regarded as the two largest deposits of the world. As in 2004, the estimated reserves in the former were 24 billion tonnes and in the latter, 18 billion tonnes (66% Fe).

In India, hematite occurs mainly as banded formations (e.g., banded hematite quartzite or BHQ) belonging to the Precambrian age, and is fairly widely distributed in the states of Jharkhand, Orissa, Chhattisgarh, Karnataka, Goa and Maharashtra. Iron ore bodies occur as pockets at the top of these formations enriched in iron due to weathering and leaching out of silica. The hematite iron ore of India is generally high-alumina and high-silica at places containing up to 6% Al_2O_3 and up to 8% SiO_2 . The other main impurity is phosphorus (up to 0.1%). The ore occurs in both ‘lumps’ and ‘fines’ forms. In some places of eastern India, very high grade ultra-fine blue dust occurs in significant quantities.

HISTORY

In the evolution of civilization, the year 1800 BC is an important milestone. Right since the palaeolithic age through the neolithic age, copper age and thereafter bronze age till 1800 BC, the entire period is referred to as “*old world*”. The oldest evidence of manufacture and use of iron dates back to the year 1800 BC, and this is regarded as the beginning of “*iron age*” and what is referred to

as the “*new world*”. Invention of iron set off a chain of technological revolutions which has been continuing ever since. But use of hematite is believed to be known to man long before the invention of iron metal. In rock paintings discovered by archaeologists in Mirzapur district of Uttar Pradesh, India and believed to be 8000 years old, various colours have been observed. It has been concluded that among different colours, different shades of red were obtained from hematite.

In the beginning of iron age, it is believed that some pure iron materials were accidentally found and such iron was used during the times of Pharaohs in Egypt. Most probably the iron was sourced to some meteorites, which used to be referred to as “*star metal*” or “*stones from heaven*” or “*gift of the gods*”. Manufacturing of iron is believed to begin in around 1200 BC. Steel making technology more or less coincided with the beginning of Christian era. In the 14th century, large scale operations started with the invention of blast furnace in Great Britain. Initially, for a couple of hundred years, wood charcoal was used as the fuel; but later on, in 1710, coal revolutionized the iron-making technology. Large scale manufacturing of steel became possible only after 1856, when Bessemer invented his conversion process.

In USA, although use of iron ore was known in 1608, organized iron industry began in 1844 after the Lake Superior deposits were discovered.

In India, iron-made weapons were mentioned in mythology, but first recorded history regarding use of iron-made weapons dates back to the time of Alexander’s invasion (326 BC). Iron casting technology was not known in those days, and canons and guns were mostly made by forging wrought iron. The iron pillar in New Delhi (310 AD) was an excellent example of forged wrought iron. Technology for melting and shaping of “*wootz*”, a kind of ultra-high carbon steel containing 1.5% carbon also known as “*Damascus steel*” or “*Ukku*” or “*Bulat*” or “*Ondanique*”, which used to be exported to Damascus from India for making ‘*Damascus swords*’, was known in India as early as 300 BC. The indigenous iron and steel industries, though small scale and unorganized, were wide spread throughout India during the ancient and Medieval periods. During 1778–1795 some sporadic operations were carried out by M/S Farquhar & Motte in Birbhum district of Bengal. Their operations were based on local methods, most probably using charcoal, and were eventually abandoned. The European methods of smelting iron ore were successfully adopted for the first time in 1830, when the India Steel Iron and Chrome Company was established by J. M. Heath and a pig iron plant based on ore from Salem district of TamilNadu, was set up in Porto Novo in South Arcot district of Tamil Nadu. These works were taken over in 1833 by Porto Novo Steel & Iron Co. and the East Indian Iron Co, who expanded the industry by starting additional pig iron plants in different places of the same state during the period 1833–1853. Pig iron from these plants were regularly shipped to Sheffield, UK for making steel which was used in construction works in UK. But due to bad financial management, the company finally closed down in 1867. During the period 1839–1875, unsuccessful attempts for manufacturing iron using charcoal, were made in Bengal, in Nainital district of present Uttaranchal state and in Indore, Madhya Pradesh. By 1875, both coal mining and coke manufacturing had commenced in Bengal, and using coke based on coal from Raniganj coal field, pig iron manufacturing was started in Kulti and Hirapur in Bengal by a private company, which was taken over by the government in 1884 and again resold in 1889 to Bengal Iron & Steel Co. Ltd. (renamed as Bengal Iron Co. Ltd. in 1919). In that plant, steel was manufactured during a brief period 1903–1905, in an open hearth furnace.

In 1911, Tata Iron & Steel Co. established its plant in Jamshedpur in present Jharkhand. This was followed by the furnaces of Indian Iron & Steel Co. at Burnpur in present West Bengal in 1922, which took over the Kulti plant of Bengal Iron Co. Ltd. in 1936. Based on pig iron produced in the Hirapur

works, Burn & Co. started manufacturing steel products at Kolkata in 1937. Meanwhile, in 1933, Mysore Government started a charcoal-based iron plant at Bhadravati in 1933. These plants kept on introducing newer and newer technologies and built the foundation of the Indian iron and steel industry before her independence in 1947.

After independence, in 1953, the Government of India set up Hindustan Steel Ltd., and three steel plants came up at Rourkela in Orissa, at Bhilai in present Chhattisgarh and at Durgapur in West Bengal. This company was later renamed as Steel Authority of India Ltd. (SAIL), and a few more plants manufacturing steel and special steels at Bokaro in present Jharkhand, at Slem in Tamil Nadu and at Chandrapur in Maharashtra were added to it. By the early 21st century, there were 11 primary iron and steel plants and a number of secondary steel plants. The production of pig iron, which was a meagre 12700 tonnes during the 5-year period 1875–1879, rose to 1.67 million tonnes of pig iron plus 1.46 million tonnes of steel ingots in 1950, and then to 4.07 million tonnes of pig iron plus 31.63 million tonnes of steel in 2001–02 compared to world steel production of 965 million tonnes during 2003.

History of iron ore (hematite) mining in India is as old as the history of iron and steel production. The recorded history of production of hematite is as follows:

1900	70000 tonnes (approximately)
1940	over 3.00 million tonnes
1950	3.14 million tonnes
1960	16.61 million tonnes
1970	31.37 million tonnes
1980	41.94 million tonnes
1990	54.58 million tonnes
April, 2000–March, 2001	80.59 million tonnes
April, 2001–March, 2002	96.96 million tonnes
April, 2004–March, 2005	142.71 million tonnes

Contrary to steel, the iron ore production of India compares better with the world production which stood at 1098 million tonnes during 2003.

CRITERIA OF USE

Hematite is used both as an ore of iron and as an industrial mineral. Its typical characteristics that make it suitable for different uses are as follows:

- (1) The chemical composition is ferric oxide (Fe_2O_3) with the highest degree of oxidation possible. The most important element in it is iron, the theoretical content of which is 70 per cent. But in nature, chemically pure hematite is difficult to mine economically due to its physical properties, and some residual impurities (e.g., Al_2O_3 , SiO_2) get into the mineral. Because of the highest degree of oxidation, this compound of iron is saturated with oxygen and it is, therefore, easier to reduce it (in case of under-saturation, the affinity between iron and oxygen is somewhat strong and it becomes relatively difficult to separate the two elements).

- (2) Physically, pure hematite is a medium hard mineral, its hardness being in the range of 5.5–6.5 in the Mohs scale. But in nature, the economically significant hematites occur near the surface as a result of erosion of silicates. Hence these hematites are softer and also porous, i.e., not very dense or compact even when they are in lumpy form. Besides, they occur also as friable ore prone to breaking into fines during mining and handling.
- (3) It is resistant to corrosion.
- (4) It has a high refractive index ranging in values from 2.94–3.22 when in the form of very thin laminae as in the case of micaceous hematite. Refractive index is a measure of the change in direction that oblique light rays undergo when travelling from air to another medium (in this case the hematite laminae) and is expressed with reference to air (refractive index practically 1). Refractive index has some relation to luster.
- (5) Although colour of hematite is dark grey to black, it is blood red when in powder form.
- (6) The micaceous hematite has a mica-like platy structure. It crumbles easily to powder.

USES

Hematite is mostly used to produce some intermediate products, and in a lesser degree, some directly usable products. These as well as the relatively less popular uses are as follows.

- (1) **Sinter:** One of the methods to convert iron ore fines is sintering. By application of just enough heat to fuse the corners of the ore particles, they are made to join together to form a lumpy mass. This product is called 'sinter'. Sinters are not very compact, having 11–18% porosity, because some corners of a particle melt, and not the entire particle. But, at the same time, they are tough enough to withstand the stress within a blast furnace. These are good substitutes of natural lumps, and can be blended with the latter in the blast furnace charge. For optimizing productivity of blast furnaces, the fluxing material i.e. limestone powder (90% (-) 3 mm size) is intimately mixed at the sintering stage itself. The limestone adds strength to the sinter if it is distributed uniformly in the matrix. This super-fluxing of sinters eliminates the need for raw limestone charge. Coke breeze (85% (-) 3 mm size), dolomite mill scales and flue dust fines along with limestone, can also be mixed to make the sinter a completely self-sufficient feed. Sinters are made on rectangular flat tops of cylinders tapering downward to grate bottoms.
- (2) **Pellets:** Very fine particles (size in microns) cannot be sintered as they will fuse altogether. So, they are formed into spherical objects called 'pellets', and the process is called pelletization. To the iron ore fines, 0.5–3.0% bentonite is added as a binder. Coke breeze and some flux (limestone) may also be added. The mixture is placed in cones, drums or discs, out of which discs are relatively more flexible with regard to types of ore and they can be controlled better. A disc pelletizer is a rotating inclined flat plate table. The particles gradually coalesce — first into very small pellets, which go on taking more and more particles and keep enlarging in size till they attain specified sizes. Water is sprayed as required. These are called green pellets, and the operation is called 'balling'. The control is effected by changing the angle (20–80°) and the r.p.m. (+8) of the disc. The green pellets are then heat treated at a temperature of above 1200°C – generally around 1315°C – in grate kilns, followed by air cooling with a view to obtaining necessary strength. Quality of pellets usable in the blast furnace is mainly determined by their characteristics of size, crushing and abrasion resistance, reducibility and the free growth and porosity index. Values of the parameters are determined through industrial scale experiments by setting the

prerequisite that when using pellets in the blast furnaces, their diameters should be in the range 9.5–25.0 mm., and within this range the size fraction 10–15 mm should represent a minimum of 85 per cent. Values of 6% for crushing and 5% for abrasion (drum values i.e., percentage of pellets not able to withstand the stress in a standard rotating drum) are considered acceptable. A reducibility index of 0.7–0.8% per minute for basic pellets is considered good. A maximum of 14% free growth index (increase in volume expressed as a percentage of initial volume under test conditions i.e., 1050°C for 30 minutes in a CO blow). Porosity should be between 20 and 30 per cent. Unlike sinter, even if limestone is added to raw mix for pellets, supplementary limestone addition in blast furnace is necessary. A minimum of 25% of pellets in the blast furnace charge has been found to have a salutary effect on productivity.

- (3) **Pig iron:** Pig iron is both an intermediate product for steel manufacturing and a material for direct use in casting (cast iron) or fabricating (wrought iron) parts of machines, structures etc. In old references, pig iron for these different types of uses used to be mentioned as ‘foundry’ and ‘basic’ grades of pig iron. Now-a-days, this classification is no longer used. A special type of low-phosphorus pig iron is used for making “*spun pipes*”.

Pig iron is produced in tall blast furnaces into which, conventionally, a charge of lumpy iron ore (either natural lumps or fines converted to this form), limestone, coke and manganese oxide is dropped from the top, and subjected to blasts of air through the sides at the lower zone; and to which some initial heat is applied. So far as natural lumps are concerned, they are seldom mined in the required grades, and it has now become an established practice to subject them to some preparation or beneficiation. The conventional methods consist of plain water washing and scrubbing, tromelling, wet screening, classification, and jigging or cycloning. But these methods achieve only limited success inasmuch as the ultra-fine grains of Al_2O_3 are not eliminated, and also considerable iron values are lost in the slimes. A specialized method consists in selective dispersion (flocculation) of aluminous gangue from a dilute slurry system using organic/inorganic additives (e.g., sodium humate, starch, polyacrylamide, phenol- and lignite-based polymer additives etc.

The reactions within a blast furnace are very complex. But the essential principle can be explained thus. The carbon of the coke reacts with the oxygen of the air to produce heat and carbon monoxide (CO). The heat melts the charge, and the CO, being unsaturated oxide, combines with the oxygen of the hematite reducing the latter to metallic iron, and generating carbon dioxide (CO_2). The impurities like SiO_2 and Al_2O_3 present in the hematite react with the limestone producing lime-alumina silicates (with heavy metal oxides) called ‘slag’ and a mixture of CO, CO_2 and NO_2 that escape as top gas. The molten slag, being lighter than and immiscible in the molten iron metal, floats on the surface of the latter. The upper layer of the molten slag is tapped out through an outlet at the upper level of the blast furnace, processed depending on its future use and stacked separately where it cools and solidifies. The molten iron of the blast furnace is transferred into the pig bed (sand moulds for ingots) or mobile ladles. In fact, the name ‘pig iron’ originated in the early days of iron ore reduction when the total output of the blast furnace was sand-cast into masses of iron resembling the shape of a reclining pig. The oldest method of pig-casting in sand beds has now been replaced by pig-casting machines.

Pig iron contains 3–4% carbon in general (may be up to 6%) besides little quantities of manganese, phosphorus, sulphur and silicon. High carbon content makes it hard and brittle. Depending on the form in which the carbon occurs within pig iron, it can be either grey pig iron, or, white pig iron. In grey pig iron, carbon is precipitated in the fractures as graphite flakes; in the white pig iron, it is dissolved as iron carbide. White pig iron is harder and more brittle in comparison to grey pig iron. Both types of pig iron are the basic raw materials for making down stream products like cast iron, wrought iron, spheroidal graphite iron and steel. The differences amongst these products lie mainly in the carbon content.

- (4) **Cast iron:** Pig iron ingot or cast iron scrap is remelted in cupola furnaces, carbon and other elements are added according to the required specification, and cast in foundry moulds in the desired shapes and sizes as per the end products. The cast iron made from white pig iron is called '*white cast iron*'; and that from grey pig iron, '*grey cast iron*'. White cast iron is used where the components require a hard wear-resistant surface. It is called '*chilled cast iron*' and is produced by sudden cooling of the melt to form a hard zone. The carbon is in the form of iron carbide and its content varies from 3–4 per cent. The other elements are silicon (0.5%), sulphur (0.1%), phosphorus (0.1%) and manganese (0.8%). It is used to make crusher jaws of rock-cutting machines, metal and paper rollers, ball milling plants etc. Grey cast iron also contains 3–4% carbon, but as graphite; other elements are silicon (2–3%), sulphur (0.08%), phosphorus (0.15%), manganese (0.8%). It is less brittle and more machinable than white cast iron, and is used for making machine bases, engine blocks, brackets, pulleys, gears etc.
- (5) **Malleable cast iron:** Malleable cast iron is produced by giving the white cast iron a modifying heat treatment involving slow heating for long duration (annealing). It is fairly ductile with 4-14% elongation (hence it is also called "*ductile iron*"), capable of withstanding suddenly applied stress, corrosion resistant, strong, tough and machinable. Carbon content in the form of iron carbide, varies from 2.5–3.0%, silicon 0.5–1.1%, sulphur 0.10–0.15%, phosphorus up to 0.1% and manganese 0.4 per cent. It is used to make transmission line hardware, water fittings, tools, conveyor links etc.
- (6) **High duty cast iron:** High duty cast irons are stronger than grey cast iron in which much of the carbon is originally in the form of coarse flakes. These contain metals like nickel, chromium, copper and also some other substances like calcium silicide, cerium or magnesium may also be added. Its carbon content may vary from 2.5–3.5 %, silicon from 1.5–2.5%, sulphur 0.02–0.1%, phosphorus from 0.02–2.0% and its manganese content is around 0.8 per cent.

If calcium silicate is added to the liquid metal, graphite is transformed into fine flakes, and the cast iron is known as "*mechanite cast iron*". It is used to make products like gears, fly wheels etc., where strength is needed.

If cerium and/or magnesium is added to the liquid metal, then the graphite is transformed to fine spheroidal form, and the cast iron is called "*spheroidal graphitic cast iron or SG cast iron*". The metal may be annealed before use, in which case the elongation increases by up to 20%, and the product is called "*ductile iron*". It is used for making crank shafts, metal working rolls and for other works where high strength is needed.

- (7) **Wrought iron :** Wrought iron is defined by American Society for Testing Materials (ASTM) as "a ferrous material, aggregated from a solidifying mass of pasty. Crystalline

particles of highly refined metallic iron, with which, without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag". The main distinguishing characteristics are: (i) carbon is practically absent, i.e. it is an almost pure form of pig iron, and (ii) it must contain some slag (1–3% ferrous silicate), which is the result of oxidizing reactions of refining, and which is uniformly distributed as minute threads imparting a fibrous structure (cf. crystalline structure of steel). Because of absence of carbon, it is highly malleable and it can be shaped into useful articles by re-heating and forging. Wrought iron was the product in use since the prehistoric age till the advent of the age of steel in 1856. The furnace used was small and the heat applied was low – up to 1500°C or so, i.e., less than the melting point of iron (1800°C). The technology was somewhat improved by H. Court in 1784. But even then it was limited by small size of the furnace (called ‘puddling furnace’) and low temperature, that could heat the mixture of ore and flux to a semisolid mass, and it required constant manual stirring for the oxidizing reactions to take place. As, unlike in steel-making, the metal and the slag were not in molten state, they could not be separated and thus the slag got thoroughly impregnated in the metal. By squeezing and rolling the semisolid mixture, the content of slag could, at best, be reduced, but not totally removed. This is how the characteristic fibrous structure was formed in wrought iron. After the advent of steel, the highly labour-intensive nature of the technology of making wrought iron and its low productivity resulted in fast obsolescence of this primitive product, but, even then, it continued to find some use where corrosion- and shock-resistance were important criteria.

- (8) **Directly reduced iron:** Directly reduced iron (solid reduction), when in lump form, is called “*sponge iron*”; when in briquette form, called “*hot briquetted iron or HBI*”; and when in liquid form, it is called simply “*hot metal*”. All these products are feedstock for steel-making in electric arc furnaces. These are produced by non-blast furnace methods, and the reduction of iron ore takes place either in solid state or in liquid phase. The technology was first tried on pilot scale in the 1920s, and the trials were intensified after 1939. At least, 32 processes have been investigated since 1939. The relatively more important and currently relevant processes can be grouped under the following generic names:

- (a) *Direct Reduction (DR):* This process is based on both coal and natural gas, and the reduction takes place in solid phase in horizontal rotary kilns. The products are sponge iron or HBI. The composition of a typical coal-based Indian sponge iron produced in a rotary kiln is: 74–80% *metallic iron*; 89–91% *total iron*; 1.8% SiO_2 ; 2.3% Al_2O_3 ; 0.25% *S*; 0.05% *P*. Wilberg-Soderfers, Midrex, Arameo, NSC, Purofer, HYL, FIOR, HIB, Knipp-Renn, Krupp-CODIR, SL/RN, INRED, ELRED, KR and Coin processes come in this group. These processes differ from each other by (i) whether reducing gas is supplied to the reduction furnace or (ii) whether reducing gas is generated within the reducing furnace or (iii) whether reduction and smelting of ore is combined in the same vessel. In a typical Indian coal-based process, a mix of iron ore, coal and dolomite (or limestone, as flux) is fed into the rotary kiln and heated at a temperature of about 1100°C; and then the output consisting of a mix of sponge iron, char and Ca/Mg oxide is subjected to magnetic separation whereby the magnetic sponge iron and the non-magnetic fraction “dolochar” comprising a mixture of char and Ca/Mg oxide are separated.

- (b) *Smelting Reduction (SR)*: This is a sophistication of the DR process by which hot metal is produced. In this technology, iron oxide reduction takes place at high temperature with a substantial part of the reduction taking place in liquid phase. In this technology, there is greater flexibility in raw material size and grade, scale of operation, furnace size etc. Here, reduction and smelting (i.e., melting accompanied by chemical reactions) of ore take place in the same vessel. Broadly, SR involves two steps: (i) removal of oxygen in solid state to varying extents, and (ii) removal of the remaining oxygen through liquid phase reduction reactions. Corex, Dios, Hismelt, Romelt, Aisi-Doe, Ausmelt, Sirosmelt and Cyclone Converter Furnace (CCF) come in this group. As in the beginning of 21st century, some of these processes are in various stages of development. Commercial plants using Corex technology are, however, in operation in South Africa and a few other countries, while one plant based on Hismelt technology is in operation at Kwinana, Australia. The key to economics lies in the utilization of the large quantities of rich high-calorie off-gases. By Hismelt technology, highly pure metal can be produced using high-phosphorus iron ore and noncoking coal.
- (c) *Plasmasmelt*: In this technology, a plasma generator generating gas at temperatures ranging from 4000–5000°C provides the thermal energy, while coal, gas or oil serves as the reductant. Iron ore is first partially in fluidized bed reactors and then fully reduced to liquid metal in a shaft furnace by the plasma and the reductant.
- (9) **Iron carbide (Fe_3C)**: Fe_3C is reduced iron oxide with 5–6% chemically fixed carbon. It is a direct feed for steel-making and it provides added energy through the in-built carbon content. It is produced in a fluidized bed reactor through a gas-solids reaction. Preheated iron oxide fines (0.1–1.0 mm size) are supported in an upward stream of gas composed of CO , CO_2 , H_2 , CH_4 and water vapour at a temperature of 550–600°C which is lower than that required by sponge iron. Hydrogen reduces iron oxide to iron which then reacts with carbonaceous gases to produce Fe_3C . The viability of the technology depends on a steady and assured supply of natural gas. Its commercial viability has not been established in India.
- (10) **Steel**: Iron and steel scrap, sponge iron, hot metallic iron and pig iron — all are processed to obtain the end product steel (also called “*plain carbon steel*”). Steel is essentially a refined alloy of iron and carbon with carbon content lower than in pig iron – generally varying from 0.01–1.7%, but it may go up to 2 per cent. Total absence of carbon would make it very soft and unusable for most of the purposes. Steel-making is, therefore, nothing but the removal, by combustion, of the carbon contained in the iron. As a result, structure of the metal becomes more resilient, more flexible, stronger and better workable than iron. Besides carbon, sulphur and phosphorus are also removed by oxidation, a little manganese and silicon are added to improve the mechanical properties of steel (if too much of these are added, then the steel would be called ‘alloy steel’). For removing the impurities, coke and flux are charged along with the pig iron. Some iron ore is also added to the charge for providing oxygen for reaction with the fuel for heat generation and better operational control by which the impurities (including those in the fuel) are removed in the form of slag.

Steel manufacturing processes: Steel can be manufactured by four processes in four types of furnaces namely (i) Open hearth converter, (ii) Bessemer converter, (iii) Basic oxygen furnace or BOF, and (iv) Electric arc furnace or EAF.

- (i) *Open hearth process:* In this process, pig iron, some scrap and limestone are placed in the hearth. A mixture of gas and air is blown over the iron which melts at 1800°C. This molten iron gets oxidized. This oxidation is also referred to as “*hearth refining*”. The oxides of the impurities react with limestone and form the slag which, being lighter, floats on the molten steel, and is drained off. Then the steel is tapped. There are some design variations in the furnace, namely, “*twin hearth furnace*” and “*KORF furnace*”.
- (ii) *Bessemer process:* It may be either ‘basic’ Bessemer process or ‘acid/conventional’ Bessemer process. In the basic process, a vessel that can be rotated on a horizontal axis, is used. Pig iron is first melted in a ladle and then loaded into it. Compressed air is blown through the molten iron from nozzles (tuyeres) in the bottom in order to oxidize the carbon and other impurities. The converter is then rotated, and first the molten slag and then the molten steel are poured out. This oxidation is also called “*air refining*”. In this case, air-blowing tends to cool and solidify the slag, but for the fact that oxidation of phosphorus in the pig iron produces additional heat. This process is therefore suitable for high phosphorus pig iron.

However, in acid or conventional Bessemer process, low phosphorus and low sulphur pig iron can be converted. In this case, the problem of maintaining temperature is solved by limiting the size of the converter and some other design changes.

- (iii) *Basic oxygen process:* In this process, pure oxygen under high pressure, instead of air, is applied to the molten pig iron. Depending on the design and position of the oxygen-blowing tube (called “*lance*”) – on sides, top etc., there are four types of converters namely, LD converter, LD-AC converter, Rotor converter and Kaldo converter. The LD-AC process has a provision for injecting limestone powder along with oxygen, and is particularly suited to high phosphorus pig iron.
- (iv) *Electric arc/induction process:* In this process, the requisite heat is not produced by the burning of gas or coal, but by an electric current – more specifically, an electric arc formed between a number of carbon electrodes and the molten bath. No air or oxygen is supplied to the furnace, and instead, iron oxide is used as the oxidizing agent. The charge consists of pig iron, iron and steel scrap, sponge iron or hot metal – independently or in combination.

Microstructure of steel: Carbon is the most important accessory element in steel, and by decreasing or increasing its content, the properties of steel can be manipulated to suit different uses. For example, increased carbon makes the steel brittle and a relatively lower content makes it tough. The form of carbon and the manner of its combination give rise to distinct microstructures of steel. The carbon in steel occurs in the form of iron carbide, which is known as “*cementite*”. The iron grains that is not combined with carbon, i.e., the grains other than cementite, are called “*ferrite*”, which is magnetic. Generally a combination of cementite and ferrite known as “*pearlite*” is present, and the steel consisting of only pearlite is called “*eutectoid steel*”. “*Austenite*” is the structure that develops when ferrite-cementite is heated to high temperature (910–1130°C), and it may remain after gradual cooling. Austenite grains are practically non-magnetic. A mixture of austenite and ferrite is called

“duplex” structure. If, however, the austenite is suddenly quenched and the quenching is continued till the temperature falls to normal, then the steel becomes hardened and the austenite changes to a new microstructure called “*martensite*”. The microstructure of fully hardened steel consists only of martensite which retains carbon in solid solution as iron carbide. However, if, instead of continuing the quenching of austenite till normal temperature, it is maintained in the range 204–399°C, then a portion of the austenite microstructure is transformed to what is known as “*bainite*”, and this process of transformation is called “*austempering*”. This process is applied to ductile iron (see ‘malleable cast iron’) to improve its properties. Austempered ductile iron is stronger than ordinary ductile iron.

Classification of steel: Depending mainly on the carbon content, steel is classified as follows:

<i>Type of steel</i>	<i>Carbon and other important elements</i>	<i>Properties</i>	<i>Principal uses</i>
(i) Mild or low carbon steel	C : 0.14–0.25% Mn : 0.4–0.8% Si : 0.15% Max P : 0.06% Max S : 0.06% Max	Very strong and fairly ductile; readily weldable, forgeable and machinable; does not fully harden on heat treatment.	Bars (flats, rounds etc.), sheet, casting, forging.
(ii) Dead soft mild steel	C : 0.06–0.14% Mn : 0.4% Max P : 0.05% Max S : 0.05% Max	Low strength; soft; highly ductile; readily forgeable and malleable in cold condition.	Suitable for application requiring forging and welding.
(iii) Free-cutting steel	C : 0.10–0.17% Mn : 0.4% Max Si : 0.1% Max P : 0.04–0.09% S : 0.20–0.35% Pb : 0.15–0.35%	Relatively low mechanical strength; readily machinable.	Suitable for use on automatic lathe machines for production of small components not requiring high mechanical strength (e.g., small screws, pins etc.).
(iv) Structural steel	C : 0.3% average Mn : 0.7% average Si : 0.1% average P : 0.05% Max S : 0.05% Max	Stronger than mild steel; low ductility; easy weldability.	Girders, beams and plates for use in buildings, bridges, ships etc.
(v) Medium carbon steel	C : 0.25–0.70% Mn : 0.6–0.9% Si : 0.15–0.30% P : 0.05% Max S : 0.05% Max	Relatively higher tensile strength, but lower ductility; poor amenability to welding; forgeable and machinable; good fatigue resistance.	Shafts and spindles of machines; crank shafts; axles; gears; forging of components of locomotives.

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<i>Type of steel</i>	<i>Carbon and other important elements</i>	<i>Properties</i>	<i>Principal uses</i>
(vi) High carbon steel	C : (+) 0.7% Mn : 0.7% average Si : 0.2% average P : 0.05% Max S : 0.05% Max	High tensile strength; hard; high resistance to wear; very low ductility; poor weldability and machinability.	These are generally used in quenched and tempered conditions. Suitable for applications requiring high wear resistance and compressive loading (e.g., bearings; leaf and large coil springs; rails of railways; wheel tires for railway coaches; wire rope).
(vii) Tool steel	C : 0.7–1.4% Mn : 0.7% average Si : 0.25% average P : 0.04% Max S : 0.04% Max	Can bear high impact loading; low Mn-content ensures minimum cracking during water-quenching and tempering.	Hand tools (e.g., axes, picks, quarrying implements); stamping dyes; metal-cutting tools.

Hot steel ingots are converted to hot rolled coils (HRC) which are thick plates or slabs used in engineering industry, boilers etc. These can also be converted to different shapes of rods, beams etc. commonly referred to as “longs”. HRC is widely traded as the primary product of steel plants, and its price is regarded as the benchmark price in international markets. The cooled HR coils become the input material for cold rolling plants where they are pressed and converted to cold rolled coils (CRC). CRC products are thin plates or sheets used in bodies of cars, refrigerators and other white goods. The CRC products are commonly referred to as “flats”. The speciality tubes used in chemicals, petroleum etc. industries require longs and the auto sector requires flats, that are made from “*extra deep drawn (or EDD)*” HR and CR coils respectively. For high performance automobile bodies, what is known as “*stamped steel*” is also used.

- (11) **Alloy steels and ferro-alloys:** An alloy is a metallic material consisting of atoms of two or more metals, or two or more elements of which most of the atoms are metal atoms. Thus, even a nonmetal can be an element in an alloy. In an alloy, the elements are admixed at the atomic level, and bulk of properties are those usually associated with metals. An alloy differs from a chemical compound inasmuch as there is no fixed formula in the former, and the contents of the elements can be varied and manipulated depending on the desirable properties to be achieved.

Advances in the steel-making technology were matched by advances in the metallurgy of steel. Plain carbon steels have been supplemented by hundreds of other types of steel using

small amounts of other elements. These are deliberate additions of materials to control the composition of the steel and to give specific desirable product qualities to suit specific uses. The role of the added materials ranges from the control of oxygen content in steel to controls of grain size, physico-mechanical properties and resistance to corrosion. The important physico-mechanical properties are hardenability (*hardenability* is different from *hardness*, and it relates to the ease with which steels will harden and the depth of hardening obtainable), stability on hardening (i.e., minimal distortion and dimensional change – important in die steels), wear resistance, toughness (i.e., shock resistance – important in construction steels, coining dies, cutting tools), hardness (important in heat-treated tool steels), grain size (i.e., fineness of grains even on over-heating), resistance to softening at elevated temperature (important in high-speed tool steels and hot-working die steels) and corrosion resistance.

Alloy steels can be ‘*low-alloy*’ and ‘*high-alloy*’. The dividing line between low-alloy and high-alloy steels is determined by the content of the added alloying elements. Up to 5% content is low and more than 5% is high.

Amongst the ferroalloys, “*ferrosilicon (FeSi)*” is somewhat special inasmuch as the alloying additive namely, silicon is a nonmetal, and also as it is not only an end product like other alloys, but is an agent for effecting de-oxidation in steel melting shop. As an alloying additive to iron, silicon increases its resistivity, and thus minimizes eddy current losses and increases magnetic permeability. Carbon is highly objectionable because it is an electrical conductor, and it will tend to produce eddy currents. Sheets of ferrosilicon (up to 5% Si with carbon practically nil) with some insulating material (often iron oxide) between them are laminated to produce transformer cores. The insulation reduces eddy current losses further. Ferrosilicon containing 84–86% Fe and 14–16% Si in powder form is used in the heavy medium mix for separation of diamond from kimberlite. The ferrosilicon helps in maintaining the specific gravity of the medium at a level of 2.7–3.0 i.e., just above that of kimberlite (2.6) and below that of diamond (3.5), without increasing the bulk, and it is also easily retrievable by magnetic separation due to its high magnetic permeability.

Besides alloys, technology has advanced to make a number of useful micro-alloys. A micro-alloy is formed by addition of ‘ppm’ quantities of an element(s) to control grain boundary composition and structure. Micro-alloying is a highly sophisticated technology.

The common alloys and their composition and uses are described in the following table.

<i>Type of alloy steel</i>	<i>Typical composition</i>	<i>Uses</i>
(1) 1.5% manganese steel	0.3% C; 1.6% Mn	Crank shafts, connecting rods, axles, high tensile bolts and studs.
(2) 1.5% manganese-molybdenum steel	0.35% C; 1.6% Mn; 0.25% Mo	Similar to above, but requiring higher tensile strength.
(3) 1% chromium-molybdenum steel	0.4% C; 0.8% Mn; 0.9% Cr; 0.2% Mo	General purpose bolts, motor axles, crank shafts etc. requiring high tensile strength.

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<i>Type of alloy steel</i>	<i>Typical composition</i>	<i>Uses</i>
(4) 3.25% nickel-chromium-molybdenum steel	0.3% C; 0.6% Mn; 2.5% Ni; 0.6% Cr; 0.6% Mo.	For withstanding severest of mechanical stresses and tempering as in axles and transmission shafts of trucks and tractors.
(5) 9% tungsten hot die steel	0.3% C; 2.5% Cr; 9.0% W.	Hot forging and punching dies for rivets; bolts; extrusion pads; die-casting dies for aluminium and copper alloys.
(6) high carbon 12% chromium die steel	2.0% C; 12.0% Cr.	Uses requiring capacity to resist corrosion and extreme pressure such as plastic-moulding dies, blanking- and press-cold-forming dies, and thread-rolling dies.
(7) 1.5% manganese non-shrink steel	0.9% C; 1.5% Mn	Uses requiring high degree of hardness and fine structure, such as taps for nonferrous metals, screw plugs, gauges, blanking press tools, broaches.
(8) silicon-chromium-tungsten shock resistant steel	0.55% C; 1.0% Cr; 2.0% W; 0.6% Si	Chisels; snap and caulking tools; heading and nail dies; engrossing punches.
(9) 18% tungsten general purpose high speed steel	0.75% C; 4.5% Cr; 18.0% W; 1.25% V.	Drills; reamers; lathe tools; broaches; milling cutters; punches; dies.
(10) 12% cobalt super high speed steel	0.8% C; 4.5% Cr; 21.0% W; 1.25% V; 12.0% Co.	Heavy duty machining on high tensile alloy steel; forged products; close-grained cast iron products; railway coach tires.
(11) Super-alloy of steel	Up to 65% Co	High temperature alloy capable of retaining its strength above 650°C; required in gas turbines, jet engines
(12) Electrical steel (also called silicon steel)	Si 0.4 - 4.5% (preferably 1.2-3.2%)	Soft magnetic material suitable for electrical applications like transformer, electric motors.
(13) Thermo-mechanically treated corrosion-resistant steel	Cu 25%	Resistant to corrosion by saline water and to rusting.
(14) Structural steel	Cu 0.35%; 0.35% Ni	Rusts very slowly by developing a relatively stable layer of hydrated iron oxide; used extensively in regions having long dry seasons; in railway coaches, garbage containers etc.

Contd.....

<i>Type of alloy steel</i>	<i>Typical composition</i>	<i>Uses</i>
(15) Pipe-line steels	Cu 0.25% ;	Retards hydrogen-induced cracking by forming thin film of copper on the surface inhibiting diffusion of hydrogen into steel. Suitable in pipelines for synthetic sea-water saturated with H ₂ S.
(16) High-strength low alloy steel	Cu 1.5%	Used in pressure vessels, off-shore platforms, naval ships.

Besides, there are some special alloys which, rather than for making end products, are used for special functional purposes to facilitate various production processes. The following is a list of such special alloys of steel along with their principal composition and the functions that they are meant for.

<i>Alloy</i>	<i>Composition</i>	<i>Function</i>
(1) Ferro-aluminium (Fe-Al)	Al 35-40% or 45-50%	De-oxidizer, de-sulphurizer and inclusion modifier for iron & steel industries; welding electrodes; hard-facing and de-oxidizing in powder form.
(2) Ferro-aluminium-calcium (Fe-Al-Ca)	Al 25-30%; Ca 15-30%	De-oxidation and modification of inclusion for better mechanical properties and avoiding nozzle clogging during continuous casting.
(3) Ferro-silico-calcium-barium (Fe-Si-Ca-Ba).	Ca 15%; Ba 15%	De-oxidizer, de-sulphurizer, inclusion modifier and inoculant for iron & steel industries.
(4) Ferro-silico-zirconium (Fe-Si-Zr)	Zr 20% or 30%	De-oxidizer, de-sulphurizer and inclusion modifier for iron & steel industries.
(5) Ferro-silico-calcium-manganese (Fe-Si-Ca-Mn).	Ca 15%; Mn 15%	De-oxidizer, de-sulphurizer and inclusion modifier for iron & steel industries.
(6) Ferro-silico-rare earth (Fe-Si-RE)	RE 30-35%	De-oxidizer, de-sulphurizer, inclusion modifier and inoculants for iron & steel industries.
(7) Ferro-silico-magnesium (Fe-Si-Mg)	Mg 5-20%; Ca and Ce if required	Spheroidizing alloy for iron.
(8) Ferro-silico-magnesium-titanium (Fe-Si-Mg-Ti)	—	Spheroidizing alloy for iron to yield compacted graphite.

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<i>Alloy</i>	<i>Composition</i>	<i>Function</i>
(9) Ferro-silico-calcium (Fe-Si-Ca)	Ca 30%; Si 60%	Modification of inclusion for better mechanical properties and avoiding nozzle clogging during continuous casting; . inoculant for iron & steel industries.
(10) Calcium-iron (Ca-Fe)	Ca 30%; Fe 70%	Modification of inclusion for better mechanical properties and avoiding nozzle clogging during continuous casting.
(11) Ferro-boron (Fe-B)	B 15-20%	Alloying addition for producing microalloy with special properties.
(12) Ferro-chromium (Fe-Cr)	Cr 60-70%	Trimming addition.
(13) Ferro-manganese (Fe-Mn)	Mn 70-85%	Trimming addition.
(14) Ferro-niobium (Fe-Nb)	Nb 60-65%	Alloying addition for imparting special properties.
(15) Ferro-vanadium (Fe-V)	V 50-55%; Al 1% Max	Alloying addition for imparting special properties.
(16) Ferro-silico-zirconium (Fe-Si-Zr)	Zr 30-35%; Si 55%	Alloying addition for imparting special properties.
(17) Ferro-titanium (Fe-Ti)	Ti 25-40%	Alloying addition for producing micro-alloys with some special properties; for welding electrodes, hard facing and de-oxidizing in powder form.
(18) Electric ferro-titanium (Fe-Ti)	Ti 65-70%	Alloying addition for producing micro-alloys with some special properties.
(19) Ferro-titanium-aluminium powder (Fe-Ti-Al)	Ti 40%; Al 10%	For welding electrodes, hard facing and de-oxidizing in powder form.
(20) Maraging steel	Ni high (12-20%); martensitic	Can be hardened and toughened by aging at moderate temperature (-500°C).
(21) Kanthal (iron-chromium-aluminium alloy)	Fe 75%; Cr 20%; Al 4.5%; Co 0.5%	Can be used in oxidizing atmosphere at high temperatures up to 1350°C as in the case of making elements in high temperature furnaces.
(22) Ferrosilicon (FeSi)	Si 5% (max); Fe 95% (min); C practically nil	Transformer cores, de-oxidant in steel-making.

Contd.....

<i>Alloy</i>	<i>Composition</i>	<i>Function</i>
(23) Hadfield steel or austenitic manganese steel	C 0.92-1.4%; Mn 12-14%; small quantities of Cr (1.8-2.2%) or Mo (0.5-2.0%) or Ni (up to 4%) or a little Al may be made	High toughness and ductility with high work hardening capability and good abrasion resistance under impact; suitable in rails, earth-moving machinery, mining machinery including rock crushers, grinding mills, dredge buckets, power shovels, bucket teeth and pumps. Addition of Cr enhances resistance to atmospheric corrosion and abrasion, that of Mo improves the toughness and resistance to cracking of castings, that of Ni stabilizes the austenite, and that of Al improves the abrasion resistance by reducing the tendency of carbon to form carbides as well as preventing the formation of martensite during quenching or deformation.
(24) High-duty aluminium bronze	Cu 79.5% ; Al 9.5%; Fe 4.5%; Ni 5.5%; Mn 1%	Superior corrosion resistance in marine conditions; also high wear resistance.
(25) High tensile brass	Cu 55%; Zn 38%; Al 2%; Fe 2%; Mn 3%	Used where high-strength castings are required, as in marine propellers.
(26) Ferrochromin	Ni 60%; Fe 25%; Cr 15%	High electrical resistance at temperatures up to 800 ⁰ C and also resistance to thermal shocks; used in heating elements of toasters, stoves etc.
(27) Incoloy	Fe 46%; Ni 32%; Cr 20.5%; Cu 0.3%; C 0.4%	Resistant to oxidation, carburization, sulphur attack at high temperature.
(28) Inconel	Ni 76%; Cr 15.8%; Fe 7.2%; Si 0.2%; Cu 0.1%; C 0.04%	Standard engineering alloy for use under severely corrosive environment.
(29) Mu-metal	Ni 77%; Fe 15%; Cu & Mo balance.	Especially high magnetic permeability; used as shield to screen magnetic fields in vacuum chambers, magnetic resonance equipment, magnetometers, magneto-encephalography.

- (12) **Stainless steel:** Stainless steel is a special type of alloy, which has come to be regarded as a distinct commodity in trade and commerce. It may be defined as alloy steels containing more than 9% chromium – with or without other elements. The other elements may include nickel, manganese, selenium, molybdenum, titanium and niobium. It is characterized by a high degree of resistance to corrosion or oxidation or rusting. In ordinary steels, the initial oxidation forms a loose permeable scale which holds moisture and allows oxygen to diffuse readily and progressively attack the metal below. In contrast, in stainless steels, the initial oxidation forms a very thin, transparent and highly adherent skin of chromium oxide

which, being impervious to oxygen, prevents progressive oxidation of the body of the stainless steel below. If nickel is also added, then the stainless steel has resistance to corrosion at high temperatures superior to that containing only chromium. The stainless steel containing only chromium has a ferritic structure while that containing both chromium and nickel has austenitic structure. The former is somewhat brittle, and the latter is relatively more workable. There may be different combinations of the two called *duplex* stainless steels.

For manufacturing stainless steel, a mixture of steel, stainless steel scrap, chromium (in the form of ferrochrome/chargechrome) and nickel (optional) is charged into an electric arc furnace (EAF) and smelted. Carbon is an important factor in stainless steel. More than 0.1% of it makes the steel hard, but it also melts in the EAF, and combines with chromium to form chromium carbide thus robbing the stainless steel of a portion of the chromium added. So, technologies of stainless steel manufacturing center around decarburization. (Decarburization is the process of removal of carbon by heating in an atmosphere in which the concentration of decarburizing gases exceeds a certain value). For decarburization there are three methods: (i) titanium or niobium is added which, having greater affinity for carbon than chromium, combines with the carbon to form stable carbide, (ii) the melt in the furnace is heated to about 1000°C (at which temperature the carbon is still in solid solution), and then rapidly cooled to prevent separation and precipitation of the carbon and formation of chromium carbide, (iii) excess chromium is added so that sufficient balance remains to impart the desired properties to the stainless steel. The technologies of *argon oxygen decarburization (AOD)* and *vacuum oxygen decarburization (VOD)* developed in the 1950s and 1960s, achieve a high level of decarburization and purity of the molten bath. In the AOD process, argon is blown into furnace to stir molten metal. This helps removal of the unwanted soluble gases as well as the undesirable consequences of oxidizing the alloying elements which takes place when carbon is lowered by regular oxygen injection. Argon is chosen because of its good electrical conductivity, low thermal conductivity and low ionization potential, and also because it is chemically inert. In the VOD process, the undesirable gases (hydrogen, nitrogen, excess oxygen etc.) are evacuated by vacuum pump and then the alloy additives are mixed.

The American Iron and Steel Institute (AISI) has allotted series of codes to different stainless steels depending on the chromium- and nickel-contents. Commonly traded and used products belong to either 400-series (containing only chromium) and 300-series (containing both chromium and nickel). The 200-series and 100-series products containing less nickel than the 300-series ones, have also been developed, but are not widely used.

Example of 400-series chromium-based stainless steels are:

<i>Chromium content</i>	<i>Other elements</i>	<i>Properties/Uses</i>
12%	0.3% C	Hard. Used in table knives.
14-18%	0.12% (max) C	Nonhardenable.
14-18%	0.12% (max)C; 0.15% (min) Se	Free machinability.
16-18%	0.95-1.20% C; 0.75% (max) Mo	Fully hardenable.
23-27%	0.2% (max) C	Resistant to scale formation when hot.
21%	0.3% Ti	Resistant to corrosion, malleable, low cost.

Examples of 300-series chromium- and nickel-based stainless steels are:

<i>Chromium content</i>	<i>Nickel content</i>	<i>Other elements</i>	<i>Properties/Uses</i>
18%	18%	0.07% C; 3.5% Mo; 0.6% Ti; 2.0% Cu	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (e.g. chemical equipment).
24-26%	19-22%	0.08% (max) C	Uses requiring resistance to scale and stress at temperatures as high as 1000 ⁰ C (e.g. staking equipment, furnace parts).
16-18%	6-8%	0.15% (max) C	Ferritic. Hardenable.
(+) 20%	Low	—	Mixture of austenite and ferrite (duplex); can be strengthened by addition of nitrogen. Very high performance stainless steel, strong, with high corrosion resistance and very good weldability. Used in appliances, in nuclear stations, in fabrication of large diameter tubes, in coins.
18-20%	8-12%	0.8% (max) C 2% Cu	Austenitic; superior corrosion resistance. Used in catering equipment.
18-20%	8-12%	0.03% (max) C	Resists formation of chromium carbide around crystal boundaries.
16-18%	10-14%	0.08% (max) C; 2-3% Mo	Superior corrosion resistance.
17-19%	9-12%	0.08% (max) C; 5-times carbon- content Ti	Resists formation of chromium carbide around crystal boundaries.
17-19%	9-13%	0.08% (max) C; 10-times carbon- content Nb	Resists formation of chromium carbide around crystal boundaries.
17%	4%	3.5% Cu	Martensitic. Used in aircraft industry.
20%	34%	3.5% Cu; 2.5% Mo	Austenitic; highly resistant to action of sulphuric acid.

Addition of nitrogen substantially increases strength, hardness and wear resistance of stainless steel without sacrificing its ductility. In a technology developed by the US Bureau of Mines in 1990, this can be done by melting and cooling the stainless steel under a high pressure (2500 times normal atmospheric pressure).

- (13) **Nitrided steels:** The nitrided steels or “*alloy nitride steels*” or “*nitralloys*” are intensely surface hardened, yet machinable. In these type of steels, a base alloy containing 0.35% Si, 0.65% Mn, 1.6% Cr, 1.1% Al, 0.2% Mo and amounts of carbon varying from 0.2 to 0.5% is processed so that nitrogen is absorbed by the surface. For this, there are two processes namely, (i) gaseous nitriding and (ii) liquid nitriding. Gaseous nitriding is carried out in a furnace through which ammonia gas is circulated ; the gas breaks down into nitrogen and hydrogen and the nitrogen is allowed to be absorbed by the surface of the alloy for 40 hours. Liquid nitriding is carried out in salt baths containing sodium cyanide heated to 510°C, and the time is varied from 30 minutes onwards depending on the depth of nitrogen absorption required.
- (14) **Glassy steel:** It is an extraordinary type of steel. Its invention as a result of research in Oak Ridge National Laboratory, USA has been reported recently in 2004. Glassy steel is more like glass than metal as the steel remains ‘glassy’ (i.e., with jumbled atomic structure) as it freezes. Glassy steel is stronger and harder than its crystalline counterpart. It is expected to be suitable for tougher medical implants and lighter aircrafts.
- (15) **Ferrites:** This ferrite is different from the ‘ferrite’ structure of steel, and is a product made from hematite. Ferrites were invented in the 1950s, and now have a very large volume share in the market. Ferrites are mixed oxide ceramics, which show magnetic properties similar to those of iron. Ferric oxide (Fe_2O_3) is a necessary component in ferrites. These are prepared by first cold or hot pressing powders of the component oxides or carbonates and pre-firing the mixture in an atmosphere of nitrogen and oxygen or air (typical ratio of $\text{N}_2:\text{O}_2$ being 5:1) at 900–1100°C; then the mixture is ground to a size of 0.1–1.0 micron, pressed and re-fired at 1100–1200°C. As for the iron oxide component, hematite fines or blue dust can be used.

The main characteristic of ferrites that distinguish them from metals is that they have high magnetic permeability like metals, and extremely high electrical resistivity like ceramics – about 10^8 – 10^{11} times that of common magnetic metals. Due to this, the energy loss on account of eddy currents is extremely small in ferrites – even at high frequencies such as microwaves, and consequently the coercive force (i.e., the demagnetizing force required to reduce magnetic flux density of a magnet to zero) and the magnetic retentivity are extremely high. This combination of properties makes ferrites unique as permanent magnets even at high frequencies extending to microwave region. Besides, ferrites are mechanically hard, and can be either strong or brittle.

There are two types of ferrites – “*soft ferrites*” and “*hard ferrites*”. The most commonly used soft ferrites are manganese-zinc ferrites ($\text{MnO}.\text{Fe}_2\text{O}_3$ 48%, $\text{ZnO}.\text{Fe}_2\text{O}_3$ 52%) and nickel-zinc ferrites ($\text{NiO}.\text{Fe}_2\text{O}_3$ 36%, $\text{ZnO}.\text{Fe}_2\text{O}_3$ 64%). Soft ferrites are hard and brittle, and hence relatively more suited to use in non-moving applications involving low wear. As for hard ferrites, they are based on sintered carbonates of barium (21%) or strontium (18%). The Curie temperature (i.e., the temperature above which a substance loses its magnetism) is relatively higher compared to that of soft ferrites. Besides, the hard ferrites are characterized by very high coercive force, and also low porosity making them less brittle and stronger than soft ferrites.

The combination of the properties – particularly the very high permanent magnetism, even at very high frequencies, and the very high electrical resistivity, make ferrites highly efficient permanent magnets at very low volumes and at low costs. On account of this, they find many special high-tech applications. Common uses of soft ferrites include radio aerials

(in antenna rods, where high sensitivity and high magnetic permeability at radio frequencies are important pre-requisites), telecommunications equipment, computer memory cores, and also tape recorders, where ferrites particles are embedded in terylene tapes. Hard ferrites are used in speakers; in cupboard door clips; in permanent magnet electric motors (e.g., wind screen wipers); in telephone receivers; in inductors and transformers; in floppy disks; in microwave circuit elements; and as deflectors on TV tubes, where high magnetic flux densities (up to 2000 gauss) at frequencies as high as 100 kilocycles per second are required for effective scanning of pictures (an average black & white television set contains approximately 340 grams of ferrites, while a colour set contains approximately 1020 grams).

(16) Iron powder: *Powder metallurgy* is the process whereby many small components are produced by fabricating metal powders or metal and ceramic powders together. Evidence of the use of powdered metals dates back to ancient times when agricultural implements and weapons were made with metal powder, mainly because powder metallurgy did not require fusion. Iron-based implements made of powder dating 300 BC have been found in Egypt. The iron pillar of Delhi dating 400 AD, was also made by this process. High quality swords are known to be made this way in Arabia during 10th/11th century. Powders may be made by the following methods.

- (a) *Chemical-electrolytic-mechanical:* The chemical methods employed are solid phase decomposition, thermal decomposition, liquid phase precipitation and gas phase precipitation. Mechanical methods include communion (i.e., size reduction), machining, milling and impact attrition.
- (b) *Atomization:* It involves creation of a fine spray of very fine droplets by subjecting a molten stream of metal to a gas or water jet under pressure. There are four variations of this technique:
 - (i) In *centrifugal atomization technique*, molten metal is ejected in the form of droplets from a rapidly spinning crucible, and almost instantaneously cooled and solidified.
 - (ii) In the *ultrasonic gas atomization technique*, disintegration of the molten stream is brought about by means of high intensity shock waves.
 - (iii) In the *rotating electrode atomization technique*, an electrode is rotated while it is melted by an electric arc, plasma arc or electric beam. The molten metal is ejected centrifugally as droplets which solidify before hitting the walls of an inert-gas-filled chamber.
 - (iv) The *vacuum atomization technique* is based on the principle that when a molten metal that is supersaturated with gas under pressure is suddenly exposed to vacuum, the gas expands and comes out of solution, causing the liquid metal to be atomized into spherical droplets.

Powder metallurgy permits the production of a broad spectrum of complex alloys with high degrees of homogeneity and fine-scale microstructure. Fabrication techniques of metal powder are as follows:

- (i) *Press and sinter:* This technique results in semi-dense parts and components. Compaction is performed in a die under high pressure (40-60 tonnes per square inch). A lubricant is mixed with the powder. The mixture is then sintered (i.e., heated to less than melting point) in order to bond the material.

- (ii) *Injection moulding*: This is employed to allow for moulding of metal and ceramic powders.
- (iii) *Hot consolidation*: By this technique, dense wrought alloys can be produced. The methods include hot isostatic pressing, powder forging, hot extrusion, dynamic compaction and powder rolling.

Iron forms the bulk of metal powders. It is made by the reduction of iron carbonyl [$\text{Fe}(\text{CO})_5$]. By powder metallurgy techniques, iron powders are used as such or to produce various alloys which, in turn, are used in various applications as follows:

- (i) Automotive and business machine components: Steel, stainless steel, iron-copper, iron-copper-carbon, iron-nickel-carbon (5% Ni), iron-nickel-molybdenum (4% Ni, 0.5% Mo), iron-nickel-manganese.
 - (ii) Permanent magnets: Aluminium-nickel-iron, aluminium-nickel-cobalt-iron.
 - (iii) Soft magnetic parts: These include pole pieces for DC-motors and generators; armatures; sintered and rolled material for use in loud speakers, radio transformers and self inductance coils. The parts are made from nickel-iron, barium-iron, zinc-iron and iron powders.
- (17) **Welding rod coating**: According to the definition of the American Welding Society, “Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal”. The mechanism of welding is based on electron emission. In this, the electron discharge takes place in the form of an arc. When electricity is passed through two electrodes (cathode and anode) in contact with each other, and then the contact is broken by moving them a little away, the resistance and consequently the potential, increases so much that the tips of the electrodes begin to glow. The temperature at the tips increases rapidly, and electron emission takes place. The high energy electrons associated with the temperature ionizes the air in the gap between the electrodes. This ionized air becomes an electrical conductor and current flows from one electrode to the other. This is the mechanism of arc discharge. The temperature of the arc may be of the order of thousands of degrees (20000–50000°C). If the broken pieces of a metal are placed in the arc, then they will fuse and join together, and this process is known as welding. The electrodes are called welding rods. If the metal to be welded itself is an electrical conductor, then it may serve as the second electrode, and only one welding rod will be required. If the welding rod is made up of a fusible metal which can mix with the fused welded metal and thus strengthen the weld, then the welding rod is called ‘consumable’ and it requires replenishment. If the welding rod remains intact and only the welded metal fuses to form the weld, then the rod is called ‘nonconsumable’. Welding may be of five types:
- (i) Arc welding
 - (ii) Electric resistance welding
 - (iii) Flame (or gas) welding
 - (iv) Forge welding
 - (v) Ultra-sound welding

Of these, the most common is arc welding. In this, electrodes (more commonly consumable) made of rods of covered metal are used. The covering serves both electrical

and metallurgical purposes. Electrically, the covering insulates the rod from accidental contact with adjacent material; metallurgically, the covering may provide gas- and slag-forming ingredients to protect the weld from the air, and it may also supply de-oxidizers or alloying material resulting in sound welds.

In one of the types of covered electrodes, the covering material consists of iron or hematite powder to the extent of 40 per cent. This serves to increase the rate of deposition of weld metal.

- (18) **Paint:** The red colour of the natural hematite, its resistance to corrosion and shining lustre (due to high refractive index), make it suitable for paint-manufacturing.
- (19) **High density aggregates (HDA) for oil pipe coating:** Hematite in ground/fine form, is useful as a high density aggregate for coating of off-shore crude oil transportation pipes.
- (20) **Cement:** Hematite in ground/fine form may be used as an additive in cement to serve the purposes of (i) balancing of the composition of the cement mix and resultant improvement in burning properties of the mix, and (ii) imparting colours.
- (21) **Audio and video cassette tapes:** These thin tapes have a polyester base, and are of low elasticity. They contain anti-static carbon molecules which prevent static electricity. For storing the recorded magnetic fields, both sides of such tapes are enriched by coatings of ferrous oxide powder.
- (22) **Nutrient:** Iron is an essential nutrient. It functions primarily as a carrier of oxygen in the body, both as a part of haemoglobin in the blood and myoglobin in the muscles. Haemoglobin is a compound containing iron porphyrin and basic protein, and it contributes 32% of mammalian erythrocytes or red cells, which, in turn, constitute 40-50% of total blood.
- (23) **Chemicals:**
- (a) *Ferric compounds:*
- (i) Ferric oxide (Fe_2O_3) or pure hematite having red streak can be used as a pigment in paint, in rouge and in polishing compounds.
 - (ii) Ferric chloride (FeCl_3) can be used as a coagulant and a mordant, and also for etching.
 - (iii) The double salt $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}(\text{SO}_4)_3]$ is one of the alums.
- (b) *Ferrous compounds:*
- (i) Hydrated ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) can be used for purifying water, in writing ink, as a greenish pigment and in medicines.
 - (ii) Mohr's salt or ferrous ammonium sulphate $[\text{Fe}(\text{SO}_4) \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$, which has a light green crystalline form, is a stable salt not oxidizing easily when exposed to air. It is used in analytical laboratories as a source of ferrous ion.
- (c) *Turnbull's blue:* It is also known as "Prussian blue". This pigment is produced from alkali ferricyanide. Ferricyanide or $[\text{Fe}(\text{CN})_6]^{3+}$ is an oxidation state of iron.
- (d) *Iron carbonyl:* Iron carbonyl or iron penta-carbonyl $[\text{Fe}(\text{CO})_5]$ is produced from direct reaction of iron with CO under pressure. It is the starting material for production of iron powders.
- (e) *Ferrocene:* First prepared in 1951, it is an organo-metallic compound of iron i.e., dicyclo pentadienyl iron $[\text{Fe}(\text{C}_5\text{H}_5)_2]$. It is formed due to reaction of cyclopentadiene

with iron oxide. Ferrocene has remarkable thermal stability and also has highly aromatic properties (cf. benzene). Its melting point is 174°C. Like benzene it can also be used as an antiknock additive to gasoline. Besides, it is a catalytic agent. Also, it has uses in fireproofing and photoimaging.

(24) **Miscellaneous uses:** Hematite is occasionally used in concrete mix and drilling mud.

SPECIFICATIONS OF USE

From the foregoing paragraphs, it is evident that there are only five important metallurgical uses of hematite beside a few non-metallurgical ones. These are:

1. Metallurgical:
 - (a) Pig iron
 - (b) Sinter
 - (c) Pellets
 - (d) Directly reduced (DR) and smelting reduced (SR) iron (sponge iron or hot briquetted iron or hot metal)
 - (e) Iron carbide (Fe_3C)
 - (f) steel
2. Non-metallurgical:
 - (a) Ferrites
 - (b) Welding rod coating
 - (c) paint
 - (d) Oil pipe coating
 - (e) Cement
 - (f) Chemicals

The other products are based on these primary products. So, specifications of hematite as such relate to these primary uses. The specifications are discussed as follows:

1. Metallurgical: The immediate products are pig iron, directly reduced (DR) iron and iron carbide, for the manufacture of which hematite ore and/or the intermediate products sinter and pellet are used in blast furnace or some other type of furnace. Ore is a natural commodity over the quality of which man has no control. Hence, the designs of furnaces and the technologies of processing have been experimented and manipulated with, to suit the grades of ore available at different places and different times, so that optimum productivity and cost-benefit ratio are achieved. So, it is more appropriate to consider the grades of ore actually used in different plants using some specific furnace-designs and some specific technologies than considering those grades as “specifications”. Ultimately, it is the economics of manufacturing of the products (which also depends on a host of other factors like logistics, taxes etc.) in a plant that determines the actual grades used, and these grades become the “specifications” for that plant.

(a) Pig iron:

- (i) *Physical specifications:* Traditionally, the most important raw material is lumpy ore, its substitutes like sinters and pellets having come later on under compulsions of economics and constraints of availability. In statistical reports of the Indian Bureau of Mines and the Central Statistical Organization, India, “*lump*” means a hard and

compact, shapeless mass of minerals, in sizes generally measured in terms of millimetres and centimetres. Technically, however, sizes of ore ranging up to 150 mm used to be referred to as lumpy hematite in early practices. Now-a-days, there has been a significant shift in the concept of size of ore desired for production of pig iron. The present demand is for hematite lump of closed size ranges in order to ensure better burden distribution and uniform permeability of the bed. The trend in the world is to use maximum-minimum ratio as 3:1, and the most preferred size range is 8–25 mm. In Japan, use of ore ranging in size from 6–30 mm (with oversize 5% max and undersize 20% max) is reported to have resulted in 3% reduction in coke rate. The current practice in India is to use lump ores in a size range of 40/30 mm to 10/6 mm. The reason is that if the size range is too wide, the spaces left by the bigger particles tend to get filled up by finer ones, and the permeability of the charge to the air blast is reduced. Besides, a charge comprising only large-sized lumps offer comparatively less surface area for reactions, and that comprising only fine-sized particles clog the furnace and do not allow free passage of the air blast.

The hardness of the lumpy ore is also important. Although many mini-blast furnaces are in operation, the conventional blast furnaces are very tall (over 30m height) to ensure economy of scale. In such tall furnaces, the burden has to fall a great deal. If the ore is not hard enough, then lots of fines will be generated inside the furnace due to friction and compressive forces to which the ore is subjected during its long descent inside the furnace. The parameters generally tested are *ASTM Tumbler Index* expressed in terms of percentage of (+)1/4 inches i.e., 6.3 mm (which is in the range of 60–70 in case of the Indian ores used, although a minimum of 80% is preferred) and the *ASTM Abrasion Index* expressed in terms of percentage of (–) 28 mesh i.e., (–) 0.5 mm (which is 10–25 in case of Indian ores used).

There is another reason why compact ore is preferred. As will be discussed later in this chapter, alumina is an undesirable component in hematite. Now, this alumina occurs dispersed in the limonitic/clayey zones as well as in the kaolinite and gibbsite which are all gangue minerals in the natural ore. More porous ore means that more leaching took place at the time of formation of the ore, and the pore spaces were filled up with aluminous clayey matter. So, higher frequency of pore spaces generally means higher alumina content.

- (ii) *Metallurgical specifications*: Through actual trials, certain metallurgical parameters for an ore to be suitable for pig iron manufacturing in a commercial blast furnace, are standardized. The common ones are “*reducibility*” and “*low temperature disintegration*”. Reducibility is a measure of acceleration in the reduction process with increase in temperature in a scale of 0–1, and the reducibility of Indian lumpy hematite ore used for pig iron manufacturing varies from 0.4–0.7. Sometimes, the term “*metallization*”, which is, in essence, reciprocal of reducibility and which is expressed in terms of percentage of ore reduced to metal, is also used. The minimum metallization preferred in Indian blast furnaces is 90 per cent. Low temperature disintegration or decrepitation is expressed in terms of two percentage figures – one for (+) 6.3 mm size, and the other for (–) 0.5 mm size, and the corresponding figures for Indian hematite are 30–40% and 15–25 per cent.

(iii) *Chemical composition*: The technologies are generally designed to suit the composition of the locally available or accessible ore, and not the other way round. The key constituent is obviously iron, but, in nature, there are different deleterious constituents also present.

Iron: Iron is the most important constituent for which the ore is valued. Theoretically, the iron content of hematite can go up to a maximum of 70%, but, in nature, it falls short of this value in varying degrees. On an average 1.5–1.7 tonnes of hematite is required to produce one tonne of pig iron. As a general rule, for every 1% increase in iron, there will be 2% increase in productivity; and 1.25–3.00% decrease in coke consumption and 25–30 kg decrease in flux consumption per tonne of ingot. In Japan, the minimum iron-content of the ore used is 63%, although 65% is preferred. The iron contents of the hematite ore actually consumed in some major blast furnaces of India are as follows :

- (1) Durgapur Steel Plant (DSP) 60–62%
- (2) Indian Iron & Steel Co (IISCO) 60–62%
- (3) Tata Iron & Steel Co (TISCO) 63–65%
- (4) Rourkela Steel Plant (RSP) 60–62%
- (5) Bhilai Steel Plant (BSP) 62–64%
- (6) Bokaro Steel Limited (BSL) 62–64%
- (7) Vishakhapatnam Steel Plant (VSP) 66.60%

It is not necessary that higher the iron content, higher will be the production of pig iron. It depends on the interplay of a host of other factors like physical properties, metallurgical characteristics and the grades of other raw materials (fuel and flux). In actual operation, the best way of comparing ores with differing iron content, is to estimate the amount of slag that is formed per tonne of pig iron. It is a fact that higher iron content need not necessarily result in lower slag volume, which also depends on the ashes in the fuel and the limestone that has to be added in order to obtain the desired slag composition. And in case the coke contains some sulphur, too low a slag volume is not desirable, because an optimum level of slag volume is needed to absorb that sulphur. In other words, the sulphur content in coke will set the minimum limit of slag volume, which in turn will set the maximum desirable limit of iron in the ore. The reason for this interrelationship between the sulphur content in coke and the slag volume is that when the sulphur is absorbed in slag, the percentage of sulphur in the latter increases, and this percentage will become higher if the slag volume is lower; with increasing sulphur percentage of slag, the efficiency of absorption of sulphur by the slag decreases, and hence the logic behind a minimum limit of slag volume for a given sulphur content in the coke.

Silica and alumina: Their individual values as well as the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio are crucial. Alumina has a high melting point and it requires more heat to melt and become fluid. Imperfect melting of the alumina results in higher viscosity of the slag. Also higher alumina indirectly engenders an increase in the volume of slag, because for every 1% increase in alumina in the ore, 35kg of extra coal and 61 kg of extra flux are consumed.

High silica, on the other hand, means more volume of slag formed directly from the silica (1.5% increase in silica causes 65 kg increase in slag volume per tonne of pig iron). Also, the slag containing only silica is acidic, but for effective de-sulphurization, basicity of the

slag should be high. For making the slag basic, lime is added, which combines with silica; and so, more silica means more lime to be added. Thus the amount of slag is further increased indirectly due to the lime. If this extra lime added is in the form of limestone, then more heat and more coal will be required to decompose it into burnt lime and CO_2 , and more coal again means more ash and more slag.

The problem of large slag volume is multiplied if alumina is high and is not completely melted, thus resulting in higher viscosity. To counter this higher viscosity, silica in the form of quartzite is added resulting in increased slag volume. Nevertheless, a little alumina (that does not require too much heat for melting) is desirable, because this fully melted alumina will then serve to increase the fluidity of the slag. Some alumina and silica are also desirable for achieving an optimum level of slag volume so as to facilitate absorption of the sulphur, if any, of the coke as discussed in the previous page. So, to sum up, ideally both alumina and silica should be low, but not too low; and there should be an optimum $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in the ore, so that addition of extraneous silica can be avoided as far as possible.

The actual contents of silica and alumina in the ores consumed in some major Indian blast furnaces are as follows:

<i>Name of plant</i>	<i>Silica (%)</i>	<i>Alumina (%)</i>
Durgapur Steel Plant (DSP)	2.5–3.5	5.5–6.0
Indian Iron & Steel Co (IISCO)	2.5	4.0–6.0
Tata Iron & Steel Co (TISCO)	Up to 2.5	Up to 3.5
Rourkela Steel Plant (RSP)	2.5–3.0	4.0–4.5
Bhilai Steel Plant (BSP)	3.0–3.5	3.25–3.75
Bokaro Steel Limited (BSL)	1.4–3.0	4.0–5.5
Visweswaraiya Iron & Steel Co (VISL)	Up to 5.0	Up to 5.0

Generally, in India, it is endeavoured to keep the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in the lumpy ore at 1.5–3.0, although, a ratio of 1–1.5 is considered ideal and desirable. In Japan, generally, the silica and alumina contents in the ore are maintained at low levels of 3% (max) and 2–3% respectively.

Phosphorus: If phosphorus is carried into the final product i.e., steel, it reduces ductility and makes the steel brittle under shocks. If its content is more than 0.2%, then the steel will be liable to crack at the time of rolling. Hence this impurity is highly objectionable. But it is also practically impossible to remove it beyond a point, because it is one of the elements which are not completely absorbed by the slag, and which remain distributed in the contact zone between molten pig iron and slag. The aim is, therefore, to remove whatever phosphorus is possible to remove economically, and for this, addition of extra flux (limestone) becomes necessary, which means increased fuel consumption and decreased productivity of the furnace. So, beyond a limit it becomes uneconomical. From this point of view, 0.2% phosphorus in the ore is generally regarded as the outermost limit. In practice,

however, the phosphorus content in the ore is kept within a much lower limit – less than 0.1%, although it depends also on the phosphorus content of the coke and other raw materials like sinters and pellets going along with the hematite. In Japan, targeted phosphorus-content in the ore is not higher than 0.06 per cent. Very low phosphorus is particularly specified if the pig iron product is meant for use in foundries and for making ductile iron spun pipes.

Sulphur: Like phosphorus, sulphur, when carried to the final product i.e., steel, produces cracks at the edges at the time of rolling of the steel. And, like phosphorus, this also is distributed in the metal-slag contact zone, and is extremely difficult as well as costly to remove beyond a certain point. In any case, it is practically impossible to bring it down to 0.05% level in the steel. It may also come from coal and other raw materials. So, sulphur content in the hematite as low as possible is preferred.

Other deleterious constituents: In hematite, there may be a few other deleterious constituents, which, although of not any significance from the Indian point of view, are nevertheless important. These are as follows:

Titanium di-oxide(TiO₂): At high temperature, a part of the TiO₂, if present in the blast furnace feed, is reduced to titanium and the latter goes into the pig iron. titanium having a strong affinity for carbon, eventually TiC is formed which has low solubility in molten pig iron. if the Ti-content of the pig iron exceeds a certain value, solid crystals of free TiC are formed; and they increase the viscosity of both pig iron and slag and they also have a tendency to form solid aggregates in the hearth of the blast furnace. The result is difficulties in tapping and other operations. For this reason, more than 2% TiO₂ is objectionable.

Zinc: It is one of the elements which is completely eliminated from both slag and metal, but still, it may give rise to problems in operating the furnace. The zinc escapes with the gas and in the upper part of the furnace, condenses as ZnO after oxidation by the CO₂. if Zn-content is too high, then the heavy layers of ZnO formed on the inside walls of the blast furnace, the charging apparatus and the gas vents may cause operating problems. A maximum of 0.2% is accepted as tolerable.

Copper: Copper is sometimes desirable in some special steels for increasing resistance to atmospheric corrosion. But, generally, if copper content in steel is more than 0.3–0.4%, it begins to cause trouble in rolling or forging at high temperature. Copper forms a low-melting alloy on the surface of the steel that penetrates the grain boundaries and makes it difficult to obtain a surface free from minute cracks.. this problem, however, is overcome if the steel also contains nickel or cobalt, equal to at least 0.5 times but not more than the amount of copper.

Arsenic: A little arsenic in the steel may be permissible, but more than 0.1% is harmful to its quality, and as most of the arsenic present in ore goes into pig iron and then into steel, it is an undesirable element in the ore.

Tin: Like arsenic, tin also is harmful to the quality of steel, and tin, if present in the ore, finds its way into the steel as it does not get removed during the processes of manufacturing pig iron and steel.

Chromium: For the production of alloy steel to which chromium is to be added, its content in the pig iron or the ore may be an advantage. But for the production of ordinary steel, it is mostly a disadvantage.

Nickel: Nickel, if present in the ore, goes completely into the pig iron in the blast furnace and it cannot be removed by oxidation during the steel-making process. In some cases, a small amount of nickel may be an advantage (e.g., when copper is present), but in other cases it is not wanted.

(b) Sinter:

This is a blast furnace feed as a substitute of lumpy hematite ore. In India, the sinters used are, generally, in the size range of 3-50 mm. These are used primarily with a view to utilizing the natural ore fines generated during mining, and the physical properties should favourably compare with those of natural lumpy ore. The sinter should be hard enough to withstand the fall during charging into the tall blast furnaces, and porous enough to offer maximum surface area for reactions to take place. In sinters, invariably some fluxing material (CaO) is added. The obvious purpose of addition of CaO is to increase efficiency of charging (in contrast to charging the flux separately) and reactions within the furnace. But another purpose is to increase strength of the sinter, which depends not only on the CaO content, but also on its uniform distribution. Further, since the process of sintering involves partial fusion of only the edges and corners of individual particles of ore. The size of the fines should not be too small to fuse completely. The preferred range of size is (-) 10 mm. To (+) 100 mesh, with undersize and oversize fractions each less than 10 per cent. The ore particles must not be sticky and so, should contain less clayey matter.

The chemical parameters of iron ore fines used for sinter manufacturing, as already mentioned, depends on local availability, overall economics of operation and productivity of the blast furnace; and the principles involved are similar to those in case of lumpy ore used directly for pig iron manufacturing. The grades of hematite fines used for sinter manufacturing in the world ranges from 62–67% Fe, and 4–8% gangue ($\text{SiO}_2 + \text{Al}_2\text{O}_3$).

Country	Fe (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	P (%)	S (%)
India	62.0–64.5	1.5–5.0	0.9–5.0	0.07	0.05
Australia	63.50	3.39	2.15	0.07	—
Brazil	64.00	4.50	1.50	0.07	0.05
Canada	66.00	4.40	0.20	0.01	0.005

Some grades of hematite produced in different countries and reported to be actually used for sinter manufacturing are as follows:

Besides physical characteristics and chemical composition, some metallurgical properties like reducibility, degradation index, cold compression strength, swelling etc. are also specified. But these are for sintered products, and not for iron ore fines as such. These properties of sinters should compare well with lumpy ore which they substitute in the blast furnace feed for pig iron manufacturing.

(c) Pellet:

Like sinters, pellets are also used as substitute of lumpy hematite in blast furnace feed for pig iron manufacturing. The advantages of using pellets lie in their uniform and controlled size, strength and composition. By their very nature and manufacturing process, they are

hard and compact with the particles well bonded. To facilitate effective bonding, sticky ore (which are unsuitable for sinter-making) and very fine sized ore are required for pellet-making. The preferred size is (-) 100 mesh (95%) and (-) 325 mesh (60–70%). At this ultra-fine size (e.g. blue dust), hematite contains a very high percentage of iron, the impurities alumina and silica getting eliminated to a large extent at a much coarser stage of size reduction during the natural process of weathering and erosion. The chemical composition of the hematite ore feed for pellets meant for use in blast furnace is:

$$\begin{aligned} \text{Fe} &: 65\% \text{ Minimum} \\ \text{SiO}_2 + \text{Al}_2\text{O}_3 &: 3\% \\ \text{P} &: 0.05\% \\ \text{S} &: 0.05\% \end{aligned}$$

In case of pellets meant for use in DR process, the grade required is still higher, because the reduction takes place in solid state without formation of any slag that could remove the impurities. The minimum iron content preferred in the ore for making such pellets is 67 per cent.

Some grades of hematite produced in different countries and reported to be actually used for pellet manufacturing are as follows:

Country	Fe (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	P (%)	S (%)
Australia	66.00	3.00	0.50	0.05	0.03
Brazil	66.50	2.00	0.75	0.07	0.05
Canada	64.90	4.71	0.50	0.01	0.002

(d) DR and SR iron:

In 1984, the Bureau of Indian Standard (BIS) prescribed a set of specifications for the direct reduction process of iron-making in general, which was partially revised in 1991. According to this, *Fe should be 65.0% minimum, SiO₂+Al₂O₃ 4.0% maximum, S 0.02% maximum, P 0.08% maximum, CaO+MgO 2.0% maximum, total of Pb, Zn, Cu, Sn, Cr, and As 0.02% maximum, size 5–25 mm (with oversize 12% and undersize 2% maximum).* Subsequently, a Task Force set up by Department of Steel, Government of India, made it more stringent. Their specifications are: *Fe 66% min, SiO₂+Al₂O₃ 4% max, S 0.02% max, P 0.04% max, size (-) 16 to (+)9 mm with oversize and undersize not more than 5% each.* But, today, with a host of new generation processes coming up in the world, this specification does not seem to carry much economic significance. These processes, each with its economic and technical advantages and disadvantages, and each with its own set of specifications regarding quality of hematite, have been and are being tried and developed. The DR process now broadly includes the smelting reduction (SR) process also. The ferrous raw material ranges from high grade lumps and pellets in COREX process to iron-bearing fines (HISMELT and FINEX processes) and steel plant waste oxides (FASTMELT, AUSMELT, TECHNORED and ROMELT processes) and even dust and sludge from blast furnaces, electric arc furnaces and pelletization plants and mill scales (FASTMELT process).

The chemical, physical and metallurgical specifications acceptable for some selected important processes are summarized below.

<i>Chemical constituent/ physical & metallurgical parameter</i>	<i>COREX process</i>	<i>Rotary kiln</i>	<i>Midrex process</i>	<i>HYL process</i>	<i>Romelt process</i>
Total iron in ore/pellet/ sinter (%)	65.00 min	64.00 min	67.00 min	65.50 min	40–45 (acceptable, but iron-bearing material containing at least 55% Fe is preferable).
SiO ₂ +Al ₂ O ₃ (%)	4.00 max	3.20 max	5.00 max	6.00 max	Relatively higher values not objectionable.
Sulphur (%)	0.004 max	0.01 max	0.015 max	0.02 max	—
Phosphorus (%)	0.08 max	0.04 max	0.015max	0.05 max	Relatively higher values not objectionable, because a high degree of de- phosphorization is achievable due to partitioning of this element in the slag and off-gases.
Na ₂ O+K ₂ O (%)	—	—	0.15 max	0.10 max	—
LOI (%)	—	—	—	1.5 max	—
Size range (mm)	10–30	6–20	6–35	6–25	Blue dust & micro- fines.
Tumbler index (% + 6.3 mm)	80–85	90.00 min	90.00 min	85.00 min	—
Abrasion index (% – 0.5 mm)	7.00 max	7.00 max	7.00 max	10.00 max	—
Metallization (%)	—	90.00 min	93.00 min	92.00 min	—
Reduction degradation index	25.0 max	7.0 max	5.0 max	20.0 max	—

Of the above processes, rotary kiln process is common in India for production of sponge iron. But, amongst the other new generation processes, only one plant (Hospet plant of Jindal Vijaynagar Steel Ltd.) based on the Corex process is in operation in India since around 2000. This plant uses noncoking coal as the fuel. The quality of lumpy hematite ore specified by this plant is: Fe 67.37%, SiO₂ 1.18%, Al₂O₃ 0.74%, P 0.06%, S 0.008 per cent. DR iron may be based on either coal or natural gas, and the percentage of iron

specified may depend upon the cost of the fuel used. For example, natural gas is costlier than coal in some places, and there, plants based on natural gas may require higher grade iron ore to offset the higher fuel cost.

So far as the rotary kiln process in India is concerned, the high percentage of iron (64% minimum) specified for the ore is, to a large extent, due to the high-ash coal being used (coal containing as high as 45% ash is actually known to be used). In fact, the three most important parameters namely, grade of iron ore, grade of coal and productivity of the kiln are interrelated.

(e) **Iron carbide (Fe_3C):**

The manufacturing process, as explained earlier under “uses”, consists in keeping the iron-bearing material in suspension by the upward forces of the reducing gases composed of CO, CO₂, H₂, CH₄ and water vapour in a fluidized bed reactor, in order to facilitate gas-solids reactions. Obviously, finer and purer the iron ore, better will be the efficiency of the reactor. So, very high grade blue dust or micro-fines are preferable.

(f) **Steel:**

Small quantities of hematite are added to the steel as a source of additional oxygen. Earlier during the 1950s and 1960s, very high grade ore containing up to over 67.5% Fe was used. Now-a-days, depending on availability, varying grades of ore are used. The grades of ore actually used in some important steel plants are as follows:

<i>Plant</i>	<i>Fe (%)</i>	<i>SiO₂ (%)</i>	<i>Al₂O₃ (%)</i>	<i>P (%)</i>	<i>Size (%)</i>
Durgapur Steel Plant (DSP)	62–63	2.5–3.5	4.5–5.0	0.01	10–50
Indian Iron & Steel Co (IISCO)	60–62	2.5	4.6	—	12–75
Tata Iron & Steel Co (TISCO)	64–65	SiO ₂ + Al ₂ O ₃ 6% max		0.05	10–40
Rourkela Steel Plant (RSP)	62–63	2.0–2.5	4.0–4.5	0.02	10–80
Bhilai Steel Plant (BSP)	64–65	3.5–5.0	3.25–3.75	0.15	10–50
Bokaro Steel Ltd (BSL)	63–64	1.5–2.0	3.5–4.0	—	10–40

2. Non-metallurgical: The non-metallurgical uses generally require high iron values of fine-sized hematite, because, it is the iron that is ultimately made use of, and in all the uses, the ore has to be ground if not in fine size.

The exception may be cement, for which a low grade ore containing 50-58% Fe is accepted by the industries. This grade very well serve their purpose, and in any case, they need only small quantities of hematite at low costs.

So far as ferrites are concerned, the objective is to achieve a combination of metallic and ceramic properties, and silica tends to decrease the ceramic properties. So, for ferrites-manufacturing, low silica hematite is required.

In case of both welding rod coating and paint, hematite containing at least 90% Fe₂O₃ is specified. Silica should not be more than 4 per cent. Sulphur and phosphorus are both highly

objectionable – for each of them the maximum limit specified is 0.015 per cent. Further, in both these uses, micaceous hematite is preferred because the flakes stick to the surfaces coated more effectively than round grains.

For the under-sea oil pipe coating, a heavy corrosion-resistant material is looked for. So it is the specific gravity of the hematite that is important. A specific gravity of at least 4.8, a minimum bulk density of 195 pounds/cu ft., and (-)10 mm size (with 5–25% of (+) 5 mm and 5–15% of (-) 0.15 mm size fractions) are generally specified by user industries in India and Middle East countries. It may be noted that to achieve this specific gravity at this fine size, ore must have more than 67% iron.

WASTE UTILIZATION

Wastes are generated right from the stage of preparation or beneficiation of lumpy ore to that of consumption of finished products. These and their potential utilization are discussed here.

- (1) **Slimes from beneficiation plants:** As has been discussed under uses of hematite for manufacturing pig iron, the lumpy ore as mined, is generally subjected to some preparation or beneficiation processes. In India, the generation of slimes from such processes is of the order of 15-18% of the ore and up to 52-62% of the iron value depending on the process deployed, may be lost in slimes. R & D studies are reportedly in progress in the laboratory of National Mineral Development Corporation (NMDC), India, to subject the slimes to further beneficiation. According to the results reported, there are possibilities of recovering up to 50% of the iron values in ultra-fine form and of blending the recovered fines with natural fines for use in industries. Besides, these slimes can be utilized for production of HBI through the Romelt process as already mentioned under the specifications for DR iron.
- (2) **Furnace and converter slags:** Slag of different compositions are generated in blast furnaces (BF), basic oxygen (LD) furnaces, electric arc furnaces (EAF) and steel melting shops (SMS) or converters. In India, in a typical integrated steel plant, about 75% of the total waste generated is accounted for by metallurgical slags; and the quantities of BF and SMS slags are in the ranges of 390–540 kg/tonne of pig iron and 180–217 kg/tonne of crude steel respectively. The potential uses of the various slags are as follows:
 - (a) *Recycling:* Of the various slags, it has been found that LD slag rich in Fe (around 20%), Ca (around 30%), Mg (around 5%) can be re-used as flux in BF and sinter plants. The magnesium content of the converter slag may be useful as a slag conditioner as well as for recycling in BF. However, the presence of high phosphorus (1.4%) is a limiting factor in these uses. For reducing phosphorus, biodephosphorization using the bacterium *Frateuria aurentia*, has been tried by the Regional Research Laboratory (RRL), Bhubaneshwar, India, and as reported by them, it is possible to remove 72–90% of the phosphorus.
 - (b) *Slag cement:* The different slags are processed to yield granulated slag, the major use of which in India is in cement making. The granulation has to be done before the slag cools down to a solid mass, because the cold solid slag is very hard and its granulation will be cost-prohibitive. Typical compositions of Indian slags and Ordinary Portland cements are:

<i>Ingredient</i>	<i>EAF slag (%)</i>	<i>Steel slag (%)</i>	<i>BF slag (%)</i>	<i>Ordinary Portland cement</i>
CaO	35–40	45–55	35–45	60–65
SiO ₂	22–25	15–18	30–40	20–22
Al ₂ O ₃	7–8	2–3	10–15	3–6
Fe ₂ O ₃	3–6	10–20	1–2	2–5
MgO	10–12	5–12	4–10	—

The advantages of mixing slag with the clinker are that it reduces the emission of CO₂, SO₂ and NO_x, and also consumption of power, fuel and labour in mining, crushing and clinkerization. In India, slag can constitute up to 55% of the raw material mix for cement. But, in this, fly ash has become a strong competitor of late.

(c) *Other uses of slag*: Concrete mix, road making, land fill, rail ballast, soil conditioner.

(3) **Dust and sludge**: The majority of dust and sludge generated within the steel plants can be recycled via sintering. If some of the dusts cannot be sintered then other agglomeration techniques have been established, by which dusts can be prepared for feeding to sinter plant or blast furnace or steel melting shop. The techniques are:

- (a) Mini pelletizer,
- (b) Cold-bonded pelletization,
- (c) Briquetting,
- (d) Oxidized pelletization,
- (e) Reduced pelletization.

In Romania, laboratory experiments were conducted on the use of powdery ferrous waste for pellet-making, by blending electrostatic filter dusts from a steel plant with iron concentrates resulting from power station ashes in suitable proportion. The mean chemical composition and grain size distributions are as follows:

<i>Type of waste</i>	<i>Fe (%)</i>	<i>SiO₂ (%)</i>	<i>Al₂O₃ (%)</i>	<i>CaO (%)</i>	<i>MnO (%)</i>	<i>P₂O₅ (%)</i>	<i>Grain size</i>
Steel shop flue dust	64.71	1.25	0.2	0.4	4.4	0.3	Up to 1.5 micrometre (91.23%)
Iron concentrate from power station ash	46.71	11.89	8.85	7.31	1.25	0.07	Up to 150 micrometre (99.98%)

Pellets were made from various blends of the finer steel shop dust and the coarser power station ash by adding bentonite (0.5–3.0%) as binder and lime (2%), and pelletizing the mixture on a rotating inclined flat plate table and finally hardening in an electric furnace at above 1200°C. It was found after the experiments that only blends containing 30% or less of power station ash met the minimum crush resistance test.

(4) **Graphite from steel-making waste**: During the 1980s, researches conducted in USA showed that high-quality graphite can be produced from a steel-making waste known as

“*kish*”. Thus, the iron and steel industry, which had historically been one of the largest consumers of graphite in USA, might, according to the researchers, prove to be the provider of a renewable source of graphite.

- (5) **Power from waste heat:** It has been found feasible to set up small power generation plants utilizing the waste heat from sponge iron kilns.
- (6) **Iron and steel scrap:** Theoretically, steel is 100% recyclable. The basic oxygen furnace (BOF) can accept up to 30% and the electric arc furnace (EAF) up to 90-100% steel scrap. According to the statistics published by the World Coal Institute (WCI), consumptions of steel scrap in the world during 2002, 2003 and 2004 were of the order of 380 million tonnes, 383 million tonnes and 400 million tonnes respectively. But the increasing complexities of materials used in consumer goods such as autos and appliances make it increasingly difficult to obtain high quality scrap from such items after they are discarded. Considerable costs have to be incurred for processing such scrap and disposing the residues. Ultimately, it is the economics that determine the use of scrap or other competing raw materials like sponge iron, pig iron etc. for steel-making.
- (7) **Defective steel ingot:** The common defects in the ingot steel may be:
 - (a) Major crackings;
 - (b) Grazings or minor crackings including hairline crackings;
 - (c) Blowholes including deep-seated ones;
 - (d) Piping or the shrinkage cavities;
 - (e) Segregation resulting from non-uniform distribution of impurities;
 - (f) Other surface defects (e.g. (i) laps or folds, (ii) defects arising from splash, bad mould surfaces, dirty or worn moulds, (iii) major pulls caused by some restriction on the free contraction of the ingot);
 - (g) Non-metallic inclusions (indigenous inclusions arising in the course of steel making and/or exogenous inclusions entrapped by the steel from mould surfaces).

When any one or more of these defects are present in the steel ingots, then the products may be considered as defective. But it is not necessary that a defective batch of steel ingot has to be discarded. There are users who may be ready to buy such ingots for some relatively ordinary usage, albeit at lower prices.

- (8) **Prevention of corrosion:** Preventing corrosion is actually waste prevention, not waste utilization as such. Corrosion is the degradation of a material by the environment, most people associate with rust. Wastage due to corrosion in terms of monetary value, has been estimated at hundreds of billions of dollars (as early as in 1922, Hadfield estimated that the annual cost of iron and steel wasted by rusting in the entire world was of the order of 600 million pounds). Some alloys of steel are corrosion resistant as discussed under alloys. But they are costlier than ordinary steel, and not always suitable for ordinary bulk usage. Pre-painting of steel products are often the answer to this problem.
- (9) **Dolochar:** The nonmagnetic fraction dolochar (a mixture of Ca/Mg oxide and char) left out after separating the magnetic sponge iron from the furnace output is considered a waste product. But it seems to have good potentiality for use in brick-making.

SUBSTITUTION

Substitution depends on the trade-off between superior performance and cost advantage. Hematite, pig iron and steel can be substituted in some of the uses depending on the economics, legislative constraints and consumer preferences. But it is not necessary that the advantages of the substitutes will remain valid all the time.

- (1) **Hematite:** Other types of iron ore like magnetite etc. may substitute hematite in iron-making, depending on local availability and price. These will be discussed later in this chapter. Besides, by-product iron ore obtained from processing of ilmenite or pyrite or pyrrhotite may also be used as a substitute.
- (2) **Pig iron:** As has been discussed under waste utilization, some types of waste like scrap etc. may sometimes substitute pig iron in steel-making.
- (3) **Steel:** In different end-uses, different materials have been tried at different times and are still being researched. These are discussed as follows:
 - (a) *Automobile engine parts:* The objective is to reduce the weight of cars without compromising the strength. Intensive researches were carried out in USA following the oil shock of the early 1970s for manufacturing lighter cars so as to achieve fuel economy. Laws were enacted in USA stipulating Corporate Average Fuel Economy (CAFÉ) Standards, and the 'miles per gallon' standards were increased compulsorily. As a result, the average US passenger car weight decreased significantly, thanks to some new materials tried in engine parts. Amongst such new materials were aluminium and magnesium. Aluminium alloys substituted steel in different small to medium sized auto parts such as radiators, pistons, pump bodies, engine covers, engine hoods etc. Magnesium alloys were used in parts like crank case, transmission housing, brake pedal support etc. Now-a-days, cars with all-aluminium engine are in the market in different countries including India.
 - (b) *Automobile bumper:* The automobile bumper is one of the examples where the material selection criteria are affected by social values, in this case, as manifested by legislation (in USA) aimed at achieving low-impact collision performance and better fuel efficiency. The bumper consists of three parts: the outer cover or fascia, the shock absorber system, and the reinforcing beam. In the early 1970s, in USA, the material normally selected for automobile bumper was metal. The bumper was basically designed to appeal to consumer aesthetics, as much as safety. Then in the mid-1970s, the US government enacted regulations requiring safety-related equipment on automobiles (e.g. head lamps, doors, leak-free fuel and cooling systems etc.) to remain operational during low-speed impact. In response to this and the Corporate Average Fuel Economy (CAFÉ) Act, researches were intensified to develop lighter, but consumer-friendly materials. The fascia market has become dominated by plastic. Although the traditional shock absorber is an all-steel stroker unit that acts much like the shock absorbers in the car suspension system, two types of plastic absorption systems have also been developed – a foam-filled cushion and a webbed egg crate design. The third bumper component, the reinforcing beam, has traditionally been a steel beam, but some glass-reinforced plastic systems have also been used. While a steel bumper tends to crease and bend due to low-impact

collision, a plastic bumper tends to bounce back with little or no damage. Even without the compulsions of legislation, there seems to be some overall cost advantage in favour of plastic bumper considering the material and fabrication costs, the fuel savings, and the low-impact repair costs.

- (c) *Automobile body panels*: The major requirements for automotive exterior body panels are low cost – including material, fabrication, assembly and tool investment costs. Exterior panels must also have an excellent painted surface finish, they must be dimensionally stable and light weight. In case of racing cars, lightness and strength – more than cost – are important considerations. Polymer composites (including fibre reinforced composite materials) and sheet moulding compounds (SMC) are superior to steel on a weight basis in applications where bending stiffness is the key design requirement, as in case of horizontal panels (e.g., hoods). Plastics have also been used for large parts of automobiles such as the side body panels. In early 2005, some scientists of USA and Australia have reported a breakthrough in research in the field of nano-technology by creating industry-ready sheets of a new material made from carbon nano-tubes having solar cell capabilities in addition to being stronger than steel or high-strength plastics, flexible and very light-weight i.e., a combination of properties looked for by manufacturers of racing car (the solar cell capability may serve the function of battery thus saving further on the weight of gasoline).
- (d) *Beverage containers*: From the manufacturers' perspective, container performance in the soft drink market is measured by the ability of the container to hold the beverage under pressure while minimizing the amount of escaping carbonation. For a small container (say 200 ml), a strong material is required, because at this size, too much carbonation tends to leak through the walls of the container, thus shortening the product's shelf life. For this size of containers, the competing materials are steel, aluminium and glass. However a life cycle analysis of the costs have made aluminium the favoured material. But, the material selection criteria change when a large sized (1 litre) container is considered. Here the amount of carbonation that leaks through plastic bottle is within acceptable limits compared to the total carbonation in the container, and therefore, plastic is the dominant material.
- (e) *Construction*: Advanced aluminium materials like "*aluminium foam*" is already replacing steel in construction in many developed countries, though it is yet to become popular in India. In water and drain waste applications, the lower cost polyvinyl chloride (PVC) pipes have largely replaced metal pipes including steel ones. pipes made of fibre glass reinforced with plastics have been used in place of mild steel pipes in tube well sinking. The advantages of plastics lie in their corrosion resistance and lightness, while their main disadvantage about which the society is now-a-days concerned, is what happens to plastic after its useful life is over, compared with the potential to recycle the metal pipe.

IRON ORE : MAGNETITE

The chemical composition of magnetite is Fe_3O_4 . A variety known as “*lodestone*” is a natural magnet. It is also called “*black ore*” due to its black colour even when it is in powder form. It occurs in granular or massive aggregate form. It is second only to hematite in usage as an ore of iron. It occurs widespread in basic igneous rocks, in banded magnetite quartzite formations (as in India) and also in titanomagnetite sand (or simply iron sand as found in New Zealand). Magnetite is the primary ore or “*protore*” of the hematite, the formation of which took place through long periods (up to 2 billion years) of alteration and enrichment. The theoretical iron content of pure magnetite is 72.4% (cf. 70% in hematite), but in nature its deposits occur in association with other impurities – particularly silica.

Magnetite is commonly mined in China, Russia, USA and Mauritania. Since 2004-05, interest is being developed in Western Australia for exploiting this mineral. In India, there is one mine namely, Kudremukh in Karnataka state, which is in the process of being closed down due to environmental problems. Besides, some stray mining of this mineral takes place in Palamou area of Jharkhand state. Also, the uranium ore of Jaduguda mine in Jharkhand state contains 2-4% magnetite, and this magnetite in fine form accounts for the rejects generated after processing of the uranium ore. These magnetite grains are suitable for use in coal washeries.

CRITERIA OF USE

- (1) *Weatherability*: Pure magnetite is hard having hardness 6, and therefore costly to crush and grind. But, since it is unsaturated with oxygen, it is prone to weathering, and when weathered, it becomes soft.
- (2) *Specific gravity*: It is quite heavy, its specific gravity being 5.18.
- (3) *Magnetic property*: In contrast to hematite, which is nonmagnetic, magnetite is strongly magnetic.
- (4) *Fracture*: Magnetite breaks in subconchoidal to uneven fracture pattern.
- (5) *Chemical composition*: Magnetite is high in iron content, and the iron is in the form Fe_3O_4 , which constitute the “*magnetics*”. Iron contents of economic magnetite deposits are mixed with silica and other impurities, and generally are in the range of 30-35 per cent. But grades as low as 16% Fe (in Turkey) and as high as 56% Fe (in Sweden and South Africa)

are also encountered. Since the bulk of the impurities comprises silica, it is relatively easy to remove it and upgrade the mineral.

USES AND SPECIFICATIONS

Magnetite may be used for metallurgical and nonmetallurgical purposes. These are as follows:

1. **Metallurgical:** Typically, magnetite iron ore deposits are characterized by low grades of 30–35% Fe with high levels of silica. The average iron-content of the ore from Kudremukh, India is 35–37%, that from Hasanselebi, Turkey is 16–22% and that of the iron sand from New Zealand is 20 per cent. Treatment process mainly involves removing of SiO₂ and producing high grade concentrate for pellet and sinter manufacturing. These final products are then used for pig iron or DR iron just as discussed in the case of hematite ore.

The first step in the process of concentration is crushing of the magnetite-bearing rock to a sufficiently fine size (– 4 mm) in order to liberate the magnetite grains. The primary crushed rock may then be subjected to gravity separation, jiggling, spiralling and shaking, tabling, drying and dry magnetic separation, followed by secondary grinding to (–) 74 micron size and wet magnetic separation. In India, the Kudremukh ore, after primary crushing, is straightway subjected to primary magnetic separation followed by regrinding and secondary magnetic separation. The nonmagnetic fraction is then subjected to gravity concentration and flotation.

Crushing/grinding of the hard primary magnetite will be very costly and uneconomic. For this reason it is the soft weathered parts of magnetite deposits or the iron sand deposits that are preferred for concentration and utilization. The weatherability of magnetite is, therefore, an important criterion for its use.

It is the magnetic property of magnetite that is made use of to separate it from the nonmagnetic silica and other impurities. Some magnetite grains may pass into the nonmagnetic fraction along with silica. Then the higher specific gravity of magnetite than that of silica is taken advantage of in gravity concentration to recover the magnetite.

The following table will give a comparative idea of the degrees of upgrading of different ores.

<i>Parameter</i>	<i>Kudremuch ore</i>		<i>Turkey ore (Pilot plant)</i>		<i>New Zealand ore</i>	
	<i>Run-of-mine</i>	<i>Concentrate</i>	<i>Bulk sample</i>	<i>Concentrate</i>	<i>Run-of-mine</i>	<i>Concentrate</i>
Fe (%)	37	67–68	16–22	69	20	59
SiO ₂ (%)	—	3.5–4.5	28–35	—	—	—
Al ₂ O ₃ (%)	—	0.35–0.40	12–13	—	—	—
Al ₂ O ₃ /SiO ₂	—	0.1	—	—	—	—
P(%)	—	0.02–0.03	—	—	—	—
Size(mm)	—	(–) 0.15 (98%)	—	(–) 0.074	—	—

Because of the fine size and high grade, the concentrates are ideally suited for pellet-making. The Kudremukh concentrates can also be blended with hematite ore fines to the extent of up to 15-20% for use as sinter feed. The typical pellets made from the Kudremukh concentrates have the following characteristics.

<i>Parameter</i>	<i>Pellet for pig iron manufacturing</i>	<i>Pellet for DR manufacturing</i>
Fe (%)	65.0–66.0	66.5–67.0
SiO ₂ (%)	3.5–4.5	2.0–2.5
Al ₂ O ₃ (%)	0.50–0.55	0.50
Al ₂ O ₃ /SiO ₂	0.15	0.20–0.25
P (%)	0.025 – 0.035	
Size (mm)	9 – 16 (90%)	
Cold compression strength (kg)	250–280	
ASTM Tumbler Index (+1/4 inch)	94–96 %	
ASTM Abrasion Index (-28 mesh)	4–6%	
Reducibility (% minimum at 40% reduction)	0.7–1.0	
Low temperature disintegration	+ 6.3 mm 90–96% – 0.5 mm 2–5%	
Swelling	12–16%	

2. Non-metallurgical:

(a) **Coal washing:** In heavy medium separation of coal from shaly matter, the principle involved is to feed the ground mixture of the two into a medium which is heavier than coal (specific gravity 1.14–1.40) but lighter than shale and other mineral matter (specific gravity 2.5–3.5), so that the coal particles can float while the shale particles sink. As for heavy medium, water containing the right proportion of fine-sized grains of magnetite in suspension (so as to achieve the right specific gravity) is used. While the shale particles sink and part of the coal particles float, many coal particles adhere to the magnetite grains. The nonmagnetic coal particles are separated from the magnetic grains of magnetite by magnetic separation process. In this use, the magnetic property of magnetite (i.e., the magnetics content) and its specific gravity

are the important criteria. Besides, naturally occurring fine grains of magnetite are preferred to reduce the cost of its grinding. In India, the finely disseminated magnetite deposits of Palamou area of Jharkhand state are popular. The Bureau of Indian Standards (BIS) has, in 1986, specified *Fe 64% min, SiO₂+Al₂O₃ 12% max, and size (-)53 microns* in magnetite meant for this use. In reality, however, it is the magnetics (i.e., Fe₃O₄) content, more than the total Fe content, that is important, because the Fe coming from any nonmagnetic compound like Fe₂O₃ or FeO is irrelevant. The minimum magnetics content preferred by the industry is 90 per cent. Further, silica is objectionable because it not only increases grinding cost, but it also reduces specific gravity and magnetic intensity. The industry prefers ore with a maximum of 2% silica. The Palamou magnetite in India contains about 70% magnetics which can be beneficiated to meet the specifications of the industry.

- (b) **Emery manufacturing:** Emery is a natural mineral comprising an intimate mixture of magnetite and corundum used in powder form for polishing, smoothing and grinding purposes. On an average, emery contains Al₂O₃ 65% min, magnetite 22% max and SiO₂ 10% max. Artificial emery powder is also prepared by mixing corundum and magnetite grains. Corundum is very hard (second hardest natural substance after diamond) and magnetite is relatively much softer. The ratio between the two components is varied to suit the hardness required for the surface to be polished. For example, glass may require a less hard abrasive substance than metals or alloys. The softer version containing more magnetite can be made into a paste and used in emery cloth. For this application, the grains of emery should be hard enough, should be able to withstand intense heat of friction, and should not be conchoidal (in that case, the sharp edges of the grains will tend to scratch the surface being ground or polished). Corundum can withstand intense heat, and both corundum and magnetite have subconchoidal to uneven fracture pattern. Silica is objectionable because its fracture pattern is conchoidal. Therefore, insofar as magnetite is concerned, its hardness and fracture pattern are the important criteria in the manufacture of artificial emery powder.

WASTE UTILIZATION

Wastes generated during concentration of magnetite-bearing rock comprise predominantly silica. These tailings can be used in road construction and back-filling of mined out areas. So far as the wastes generated during post-concentration processes and uses are concerned, their utilization has been discussed under the chapter on hematite.

IRON ORE : SIDERITE

It is also known as “*chalybite*”. Its composition is FeCO_3 . It occurs as sedimentary deposits or hydrothermal veins (igneous), formed due to action of iron-bearing solutions on limestone. Pure siderite contains 48.2% Fe and 37.9% CO_2 , but in nature, it occurs mixed with thin beds of shale, clay or coal in sedimentary beds, or with various gangue minerals in igneous deposits. The commercial ore deposits are of sedimentary type and has been variously named as “*spathic iron ore*” (‘*spathic*’ literally means ‘layered’) and “*black band ore*” (dark bands of siderite in shale closely associated with coal seams)

Siderite is not an ore of iron from the Indian point of view, but it is an important iron ore mined in some European countries like Germany, UK and Spain. India, however, uses a small quantity of siderite for nonmetallurgical purpose.

USES AND SPECIFICATIONS

Siderite contains a fairly good percentage of iron, which can be upgraded further. When calcined at 1000°C , the CO_2 escapes leaving behind a hard spongy mass of FeO , which does not sinter at this temperature. It has hardness in the range of 3.5–4.0. These properties make it suitable for the following uses.

1. **Metallurgical:** The ore is ground, calcined and concentrated. The concentrate is then used to make pellets for use in manufacturing of iron as in the case of magnetite. Its comparatively low hardness renders grinding economic. Siderite works out to be an economic ore where commercially viable deposits of neither hematite nor magnetite are available.
2. **Hydrogenation:** Siderite is very well suited for this nonmetallurgical use on account of the hard spongy nature of its calcined product. Hydrogenation is a process by which substances chemically react with molecular hydrogen in the presence of a catalyst. In India, its main application is in Vanaspati (vegetable oil) manufacturing. Hydrogenation hardens and solidifies the liquid Vanaspati by converting the glycerides of unsaturated fatty acids (e.g., oleic and linoleic acids) to saturated ones in the presence of a nickel catalyst. The other applications of hydrogenation are in synthesis of methanol, liquid fuels, nylons and in manufacturing of various industrial organic chemical products like fatty alcohols, cyclohexanol, cyclohexane, hexamethylenediamine.

The role of siderite is in production of the hydrogen needed for hydrogenation. Siderite is calcined, and producer gas (a mixture of CO and water vapour) at a temperature of 700-1000°C is passed through pieces of the spongy residue (FeO) in sizes 1–2.5 inches, followed by a stream of steam. FeO is reduced by CO to iron, which reacts with H₂O of the steam to form FeO and release hydrogen. The hydrogen then becomes available for hydrogenation, while the FeO is re-used.

The spongy nature of the calcined siderite offers maximum surface area for the reactions to take place efficiently. Both the CO₂-content and the iron-content are, therefore, important. The former is responsible for the porosity, while the latter is responsible for the actual reduction of H₂O to hydrogen. In India, the vanaspati industry prefers a minimum of 40% iron content and about 35-40% CO₂- content, which is equivalent to around 87% FeCO₃; CaCO₃, MgCO₃ and SiO₂ are undesirable constituents, because the CaO and MgO left after calcination of the two carbonates and the SiO₂ becoming molten at the high temperature, may clog the pores of the siderite. These constituents should, therefore, be as low as possible.

In the production of hydrogen, hematite may be an inferior substitute of siderite.

IRON ORE : TACONITE

Taconite is the name given to fine-grained compact siliceous iron formations – ferruginous chert or ferruginous slate — containing very finely disseminated oxides of iron, less than 20 mesh in size. It is not an ore of iron from the Indian point of view, but large deposits occur in the Lake Superior district of USA, where it has become a second rung source of iron. Commercial deposits were formed due to natural weathering of original iron formations comprising interbedded chert, hematite and magnetite. The iron content in the taconite is low – in the range of 20-27%, rarely going up to 30 per cent.

Taconite occurs in nature in two forms, namely “*slaty taconite*” and “*cherty taconite*”. Slaty taconite is extremely finegrained and nonmagnetic. Cherty taconite consists of two fractions – magnetic and nonmagnetic. Taconite cannot be beneficiated by simple methods comprising crushing, screening, washing, jigging, drying etc. The nonmagnetic slaty type of taconite needs grinding to micron sizes, reduction roasting converting the iron to artificial magnetite, and then magnetic separation followed by flotation and filtration. So far as cherty taconite is concerned, it is first ground to 100-150 mesh size and then the magnetic and nonmagnetic fractions are separated by magnetic separation technique. The concentrates containing about 63% Fe, are agglomerated into pellets. The further use of the taconite pellets for iron-manufacturing is as in the cases of hematite or magnetite.

IRON ORE : OTHERS

There are some iron minerals which, though not considered as ore of iron in India, may nevertheless serve as commercial sources of iron in countries deficient in conventional iron ores. These are as follows:

LIMONITE

Limonite is an amorphous hydroxide of iron having chemical composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Iron accounts for 59–63% of this mineral. It is formed from pre-existing iron-bearing minerals like hematite, siderite, magnetite, and (less commonly) pyrite, mica, pyroxenite, hornblende etc. by secondary alteration through exposure to moisture or air combined with action of carbonic or organic acids. It is dark brown to black in colour, and it is also called “*brown iron ore*”. In nature it occurs admixed with hematite, clay and manganese oxides. It is an important source of iron in some European countries. Recently, towards the end of 2004, an old limonite mine (50% Fe grade) in North Korea has been readied for re-opening for mining.

GOETHITE

Goethite, named after the German poet philosopher Goethe, is also a hydroxide of iron having chemical composition $\text{FeO}(\text{OH})$. Unlike limonite, it is crystalline and light to dark brown in colour with yellowish brown streak. It is formed due to oxidation of iron-bearing minerals, and it is a major constituent of *gossan*. It may also form as the residual iron from weathering serpentine. The oolitic variety of goethite is called “*minette*”. When it occurs in large masses, it can be an economic source of iron as in the case of the Minette deposits of the Alsace-Lorraine region of France and those of Luxemburg. It may also be used as a yellow pigment.

BOG IRON ORE

The chemical composition of bog iron ore is $\text{Fe}_3(\text{OH})_6$. Goethite may be deposited in marshes and stagnant pools of water and become transformed to bog iron ore. It is loose and porous, and it may have entrapped in it petrifying leaves, wood, nuts etc. It is mined in some European countries like Netherlands, Denmark and Sweden, and $\text{Fe}_3(\text{OH})_6$ content generally ranges from 63-68 per cent. Although it may be used as an ore of iron if occurring in large masses, its principal use is

nonmetallurgical – for purification of coal gas and other industrial gases by removing sulphuretted hydrogen. For this industrial use, synthetic bog iron, developed in the 1960s by the Central Fuel Research Institute, India, is an effective substitute.

CLAY IRONSTONE

Clay ironstone is a general term given to a ferruginous mineral occurring in the form of concretionary structures embedded in beds of clay or shale. The ferruginous mineral may be either siderite or hematite or limonite. It is believed that the limonitic clay ironstone found in Damodar valley coalfield served as a source of iron during the beginning period of Indian iron industry i.e., the late 19th and early 20th centuries. It can be used as a possible substitute of bog iron ore in desulphurization of industrial gases.

LITHIUM MINERALS AND METAL

Lithium is one of the 5 alkali metals namely lithium, cesium, rubidium, sodium and potassium. Lithium is also the lightest amongst the metals. It was discovered in the beginning of nineteenth century. The commercial sources of lithium are spodumene ($\text{LiAlSi}_2\text{O}_6$) containing 4 – 8% Li_2O , petalite ($\text{LiAlSi}_4\text{O}_{10}$) containing 2-4% Li_2O , lepidolite [$\text{K}_2 \text{Li}_3\text{Al}_4 \text{Si}_7\text{O}_{21} (\text{OH},\text{F}_3)$] containing 3-4% Li_2O , and amblygonite (LiAlFPO_4) containing 8-10% Li_2O .

Recently, lithium mica mineral, zinnwaldite [$(\text{K},\text{Li})_3\text{FeAl}_3\text{Si}_5\text{O}_{16}(\text{OH},\text{F})$] has been reported in the tungsten-bearing granite rocks in Degana, India. In this rock, lithium content varies from 0.015 to 0.18 per cent. Besides, sea water and bittern contain lithium of the order of 0.2 ppm and 8 ppm respectively. In USA, lithium is recovered as phosphate from Desert Lake brines of California as a byproduct of potash and borax. In India, crude borax deposit of Pugga Valley, Ladakh contains upto 0.36% LiCl whereas the brine from Sambar Lake, Rajasthan contains 16 ppm LiCl .

RECOVERY

Lithium alumino-silicate complex is first mixed with limestone and CaCl_2 (which act as fluxes) and then calcined at high temperature. As a result it breaks up. The calcined powder is leached with water to obtain a leach solution which contains calcium and alkali chlorides. The CaCl_2 is then precipitated by adding Na_2CO_3 solution and the purified solution is concentrated through evaporation as a result of which NaCl crystallizes and precipitates. It is then filtered out. To the filtrate containing LiCl , soda ash is added and the precipitate of Li_2CO_3 is recovered as residue after filtration. The filtrate is further processed to recover lithium as fluoride or phosphate. Lithium metal can be produced by electrolysis of a fused mixture of LiCl with KCl .

CRITERIA OF USE

- (1) **Specific gravity:** Lithium metal is the lightest of all solid elements having specific gravity of about 0.534 and atomic weight of 6.94.
- (2) **Melting and boiling points:** It has a somewhat low melting point of 179°C (In terms of fluxing power 1 Kg of Li_2O is equivalent to 2 Kg of Na_2O or 3.1 Kg of K_2O). It remains liquid through a wide range of temperature from 179°C (melting point) to 1317°C (boiling point).
- (3) **Viscosity:** Its viscosity is low (due to high mobility of ions).

- (4) **Thermal conductivity:** Its thermal conductivity is high.
- (5) **Thermal expansion:** Thermal expansion co-efficient of lithium metal is relatively low. Besides, spodumene, when heated, is transformed into what is known as 'beta-spodumene'. This beta-spodumene has a very low thermal expansion co-efficient.
- (6) **Specific heat:** Its specific heat is high. In simple words, relatively more quantity of heat is required to raise the temperature of a mass of lithium metal. It is also called heat capacity.
- (7) **Electrochemical properties:** It is a good ionic conductor. Its standard potential and electrochemical equivalence are higher than all other metals.
- (8) **Optical properties:** The mineral lepidolite has refractive index 1.6 i.e., higher than that of ordinary glass (1.52).
- (9) **Chemical reactivity:** Lithium metal is highly reactive and reacts easily with other elements and compounds to form various lithium compounds, some of which have their own characteristic properties besides those of lithium metal. For example the chloride and bromide of lithium are the most hygroscopic of all inorganic compounds. The other common and useful compounds are lithium hydroxide, lithium perchlorate, lithium fluoride, lithium urate, lithium deuteride. Lithium hydroxide is very strongly alkaline.

USES

Lithium is used in all 3 forms — natural mineral, metal and chemical compounds of the metal. The common uses are as follows:

1. **Glass:** Spodumene, lepidolite and petalite are added to the raw material mix. These minerals carry some of the properties of lithium metal such as low melting point, high boiling point, high specific heat, low thermal expansion co-efficient, lightness. Besides, lepidolite has a higher refractive index than ordinary glass. Due to low melting point, these lithium minerals act as fluxing agents. In case lepidolite is used, its contained fluorine adds to the fluxing efficiency and the easy meltability prevents devitrification of molten glass. Lithium minerals may be added for this purpose to the glass-making batch to the extent of 0.1 to 0.3%, and this may result in saving of fuel up to 8 per cent. Due to high specific heat, high thermal conductivity and low thermal expansion co-efficient, the glass product attains thermal stability and is able to withstand thermal shocks. In other words the glass becomes tougher and less brittle. The relatively higher refractive index of lepidolite improves the transparency of glass. The low specific gravity of lithium makes the glass light. The wide difference between melting and boiling points of lithium combined with low viscosity helps the molten glass to attain a smooth surface finish.

To sum up, addition of lithium minerals helps in making of light, thermally stable and tough glass with relatively high refractive index and smooth surface finish. For ordinary container glass, petalite containing 1.8% Li_2O is enough, but for heat-resistant oven ware and speciality glass higher content of 4.3–4.4% is desirable (besides low alkalis 0.15% K_2O and 0.35% Na_2O). For TV tube cells, fibre glass etc, high grade concentrate of spodumene containing 7.3% Li_2O , 0.08% K_2O , 0.10% Na_2O is generally specified. Fe_2O_3 is a deleterious constituent in any glass and the lithium mineral should not contain more than 0.05% per cent.

2. **Ceramics:** Mainly the minerals spodumene and petalite and the compound lithium carbonate are preferred in manufacturing of ceramic and also glazing materials. These

minerals by virtue of their chemical composition, add Al_2O_3 to the raw material mix and also imparts thermal shock resistance to the product due to low thermal expansion coefficient of lithium as well as beta-spodumene. For use in heat resistant ceramics, high grade concentrate of spodumene containing 7.3% Li_2O , 0.08% K_2O , 0.10% Na_2O is generally specified.

3. **Lithium electrochemical cell:** Also called *lithium cell*, this is an improved version of ordinary dry cell (see chapter on manganese ore). It belongs to the primary type, which are discharged to exhaustion only once. In this cell, the anode comprises lithium metal or an alloy of lithium and aluminium (1% max) and the cathode is made up of lithiated electrolytic manganese dioxide (EMD). A lithiated MnO_2 for use in this type of cells is prepared by treating EMD with a liquid source of lithium cations that can include an aqueous solution of a lithium base or a low melting point lithium salt. The lithium cations get inserted in the crystal lattice of EMD after displacing H ion originally residing there. These cells exhibit increased operating voltage and high low temperature performance, and are also very light, efficient and long lasting. Low specific gravity, high reactivity (with the electrolyte), good mobility of ions and good electrical conductivity, high standard potential and high electro-chemical equivalence are the key criteria.
4. **Rechargeable lithium cell or Edison cell:** This is a secondary or rechargeable cell. In contrast to the primary cells (e.g. Leclanche cell) which are discharged to exhaustion only once, the secondary cells can be discharged and recharged multiple times. These are used in mine locomotives, fire alarm systems, rail and road signals, laptops, video cameras, cell phones etc. These are characterized by light weight and long life. In Edison cell, the anode is made of nickelous hydroxide (NiO.OH), the cathode comprises metallic iron in finely powdered form, while a mixture of KOH and LiOH constitute the electrolyte. In effect, during discharge, the water of the electrolyte splits into 'H' and 'OH', the 'H' reacting with 'NiOOH' to form Ni(OH)_2 and the 'OH' reacting with 'Fe' to form Fe(OH)_2 . In the process electrons are liberated and electricity generated. But 'Li' being highly reactive, it immediately reacts back with the Ni(OH)_2 and Fe(OH)_2 and the original configuration of the system is restored. This alternate charging and discharging goes on with the result that the cell has a long life. LiOH being solid powder, it forms a paste with the KOH solution, and also lithium is very light. Thus addition of LiOH to the electrolyte makes the cell light, long lasting and easy to handle. In addition, such cells can function at very low temperature – (–) 40°C , and this property coupled with lightness has been made use of in fitting them in Global Positioning System (GPS) receivers for measuring the altitude of Mt. Everest.
5. **Rocket fuel:** Lithium perchlorate is used in the solid propellant rocket mixture as a carrier and deliverer of oxygen. Due to low atomic weight of lithium, more oxygen is held in a given volume than in case of any other perchlorate.
6. **Balloon:** Lithium hydride (LiH) is used as a compact source of hydrogen which is used for inflating balloons. Due to low atomic weight of lithium, relatively more mass of hydrogen can be held in a small volume. Such balloons are used for military purpose.
7. **Air conditioner:** In this the chloride or the bromide of lithium is used for the purpose of humidity control, these halides being strongly hygroscopic.
8. **Welding & brazing:** In this application, the chloride or the fluoride of lithium is used. Like lithium metal, these compounds have also relatively low melting points and high

boiling point. Besides, these compounds are good solvents of metallic oxides. Consequently they are used as fluxing agents in welding or brazing of aluminium, magnesium and titanium metals.

9. **Medicine:** Lithium carbonate and lithium citrate are used in treatment of gout and gravels which are caused due to formation of insoluble urates from uric acid. These compounds of lithium are introduced into the body. They react with uric acid to form lithium urate which, being one of the most soluble salts of uric acid, dissolves away.
10. **Lubricant:** The starting material is lithium hydroxide (LiOH), from which lithium monohydrate (LiOH.H₂O) is formed. This monohydrate is cooked with natural fat. Due to high reactivity, it combines with the stearic acid contained in natural fat, and forms lithium stearate (also known as '*metallic soap*'). Lithium stearate is a good gelling (or thickening) agent to transfer oil into lubricating grease. This lithium-based lubricating grease has a high temperature resistance properties (due to high specific heat of lithium) and also good low temperature and water resistance properties.
11. **Metallurgy:** Due to high chemical reactivity, lithium metal is used for degassing, deoxidizing and purifying copper and bronze during refining.
12. **Weldite:** It is an alloy of aluminium and lithium and the strongest known wrought aluminium product. It maintains superior strength over a wide range of temperatures encountered in space applications. Besides, it is light weight (due to lithium content) and is weldable. It is suitable for use in oxidizer tanks in space vehicles.
13. **Electro-optical modulator:** These modulators are devices for converting electrical signals into modulated optical ones in transmission of information through optical fibres. Electro-optical fibres are made from a chemical crystal of lithium niobate. They switch laser light alternately from bright to dark and vice-versa, each change representing one digital 'bit' of information. But the lithium-based modulator suffers from the disadvantage that it requires 5 volts for its operation, and this voltage creates enough heat to disrupt and slow down data flow. Now, a substitute called "*opto-chip*" has been developed which can function at as little as 0.8 volts and is capable of switching signals at rates up to 100 GB per second.
14. **Other uses:**
 - (i) Thermonuclear fusion bomb: This is a potential use of deuteride of Li, which can be converted into two atoms of helium in a thermonuclear reaction accompanied by release of energy.
 - (ii) Industrial drying: The chloride or the bromide of lithium is used due to their strong hygroscopic property.

MANGANESE ORE

Manganese is the twelfth most abundant element in the earth's crust, the average incidence being 0.1 per cent. In nature, it occurs in one of the four types of deposits, *i.e.*, (i) sedimentary, (ii) residual, (iii) metamorphosed, and (iv) hydrothermal. Out of these, the first three types are of economic significance. Its minerals comprise oxides, carbonates and silicates. Dana has listed 138 minerals of manganese, out of which the commercial ores are pyrolusite (MnO_2 ; 63% Mn), cryptomelane (poorly developed crystalline form of pyrolusite), manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$; 62.4% Mn), psilomelane (colloidal mixture of MnO, MnO_2 and H_2O in varying proportions sometimes containing absorbed oxides of Ba, K and Na; 45-60% Mn), hausmanite (Mn_3O_4 ; 72.5% Mn), rhodochrosite (MnCO_3 ; 47.6% Mn), rhodonite (MnSiO_3 ; 41.9% Mn), bementite ($2\text{MnSiO}_3 \cdot \text{H}_2\text{O}$; 39.1% Mn), braunite ($3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$; 62% Mn, 1-7% Fe, 10% SiO_2), sitaparite ($9\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3 \cdot \text{MnO}_2 \cdot 3\text{CaO}$; 44.09% Mn, 19.32% Fe), hollandite (manganate of Mn, Ba, ferric iron; 45-50% Mn, 3-7% Fe), jacobsite ($(\text{Mn}, \text{Mg})\text{O} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$), vedenburgite ($3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$), wad (amorphous, earthy, loosely aggregated matter decomposed from oxides).

In India, it occurs either interbedded with Archaean rocks including Gondites (most of the manganese deposits as in Jharkhand, Orissa, Madhya Pradesh, Maharashtra, Karnataka), or associated with Kodurites (the relatively less important deposits of Srikakulam district, Andhra Pradesh) or lateritoid/surface enrichments over the primary deposits. The most predominant mineral is psilomelane followed by braunite. The other minerals found in India are hollandite, jacobsite, hausmanite, vedenburgite, sitaparite, pyrolusite, cryptomelane and wad. The manganese ore occurs invariably as mixtures of different manganese minerals containing varying amounts of Mn, Fe and SiO_2 . The ores are therefore described in terms of contents of these components instead of specific minerals. But pyrolusite is an exception. It is called "*manganese dioxide ore*" in India, and its commercial value depends not on manganese content alone, but on the available oxygen as well, *i.e.*, in other words, on the MnO_2 - content. The Bureau of Indian Standards (BIS), in 1986, has specified 25% as the minimum cut-off Mn-content for an ore to qualify as manganese ore, and those containing less than 25% Mn (at least 10% Mn and 55% Mn+Fe) are manganiferous iron ore. The Indian manganese ores are classified as:

- (1) Manganese ore containing 35% and more Mn,
- (2) Ferruginous manganese ore containing 25 to less than 35% Mn with minimum 48% (Fe + Mn),
- (3) Siliceous manganese ore containing 25 to less than 30% Mn and minimum 15% SiO_2 ,

(4) Manganese dioxide ore (*i.e.*, pyrolusite) containing minimum 78% MnO₂.

Sea nodules are now-a-days receiving considerable attention. Some of the nodules, *inter alia*, contain up to 32% manganese, and are regarded as a possible future source of this metal.

HISTORY

Manganese metal was first isolated by Gahn in 1774. But record of production of its ore is not available till 1890. The annual world production during that year was about 0.5 million tonnes which rose steadily to 3.6 million tonnes in 1929, 4.85 million tonnes during the years 1934-36, and then 6 million tonnes in 1937 with ups and downs during the World War-I and the Great Depression. In the year 2000, it reached the level of 19.90 million tonnes, and in 2001, it stood at the level of 22.6 million tonnes.

Although, manganese was first known in India in 1774, the history of manganese industry in India can be traced back to 1885 when the Geological Survey of India investigated a mineral which had been extensively used locally as a road metal in Srikakulam area and identified it as psilomelane. In 1891, a syndicate was formed to mine the Kodur deposit of Srikakulam district, and this was followed by establishment of Vizianagram Mining Company. In central India, the Central India Prospecting Syndicate started prospecting and mining of the deposits of Mansar, Balaghat, and Bhandara areas during the period 1899-1903. This company was renamed as Central Provinces Manganese Company Limited in 1924. Meanwhile, in 1905, Shivarajpur Syndicate started mining operations in Shivarajpur deposit of Gujarat; in 1906, the Peninsular Minerals Company of Mysore Limited began mining in Tumkur-Chitradurga belt of Karnataka state; and in 1907, the Shimoga Mineral Company Limited took up mining of the deposits of Shimoga district of the same state. With the commencement of production of manganese ore in 1891, India entered the world trade in this commodity, and the entire production continued to be export-oriented till October, 1915 when the first ferromanganese plant was commissioned by Tata Iron & Steel Co. (TISCO), followed by another plant by Bengal Iron Company Limited in November the same year. The Central Provinces Manganese Company Ltd was taken over by the Government of the independent India in June, 1962, renamed as Manganese Ore India Ltd. (MOIL) and this company remains the dominant producer of manganese ore in India ever since. The production of manganese ore in India since 1914 is as follows:

1916	0.6 million tonnes approximately
1927	1.13 million tonnes approximately
1932	0.59 million tonnes
1937	1.05 million tonnes
1946	0.28 million tonnes
1947	0.47 million tonnes
1950	0.94 million tonnes
1960	1.45 million tonnes
1970	1.70 million tonnes
1980	1.70 million tonnes
1990	1.39 million tonnes
April, 2000–March, 2001	1.60 million tonnes
April, 2002–March, 2003	1.66 million tonnes

India's manganese mining industry has all along been export-oriented even after the commencement of ferromanganese production in 1915. The annual ferromanganese production in India varied between 300 tonnes and 16000 tonnes during the pre-independence period (1915-1947), with the peak production recorded during 1939-1943 mainly due to the war time demand. The production of ferromanganese during the post-independence period is as follows:

1948	9286 tonnes
1950	15291 tonnes
1960	85677 tonnes
1970	175612 tonnes
1980	158303 tonnes
1990	203311 tonnes
April, 2001-March, 02	207000 tonnes

In the world ferromanganese production, India's contribution may not be very significant, but India ranks 7th in the world manganese ore production.

CRITERIA OF USE

- (1) **Physico-chemical characteristic of psilomelane:** Psilomelane is formed as a massive mineral by coagulation of a heterogeneous mixture of submicroscopic particles of mineral matter held in colloidal solution by water. Thus, psilomelane is what is known as a "mineral gel" or "hydrogel", and, in nature, it has some water molecules trapped within it. Whenever some changes in the external conditions take place, it loses some water molecules, and the structure of the remaining material becomes porous and finely divided, which enables it to adsorb foreign materials. This also enables psilomelane to take away oxygen and sulphur from the bath in blast furnaces.
- (2) **Desulphurizing ability of rhodochrosite:** Rhodochrosite (MnCO_3) has a stronger affinity for sulphur than for (CO_3) radical, and hence can act as an effective desulphurizer.
- (3) **De-oxidizing and De-sulphurizing ability of manganese:** Compared to iron and the nonferrous metals, manganese metal has a stronger affinity for both sulphur and oxygen.
- (4) **Colour:** Pyrolusite (MnO_2) is a strong colouring agent. In small quantities it produces a pink colour, and in large quantities it produces a black colour.
- (5) **Fusibility:** Manganese melts at a temperature of 1244°C .
- (6) **Alloying properties:** The metal manganese alloys easily with iron, and improves *hardenability* of the latter (*hardenability* is different from *hardness*, and it relates to the ease with which steels will harden and the depth of hardening obtainable). It increases the elastic limit, tenacity, strength and toughness of steel, and it raises the temperature to which it is safe to heat steel without reducing its strength.
- (7) **Medicinal properties:** Manganese oxides impart to the humans, animals and plants ability to combat some diseases.
- (8) **Chemical composition of pyrolusite:** The theoretical formula of manganese oxide is MnO , which is a stable oxide. In pyrolusite, whose chemical composition is MnO_2 , oxygen in excess of that required by the formula, is held in solid solution. Under certain conditions, this extra oxygen becomes available for oxidation reaction.

- (9) **Molecular structure of pyrolusite crystals:** Pyrolusite is dimorphous. In other words the chemical compound MnO_2 crystallizes in two genetically distinct forms – tetragonal and orthorhombic – each having different molecular structures. There is a third hexagonal form called “*akhtenskite*”, but this is extremely rare. The orthorhombic form, which is relatively rare in nature, is also called “*ramsdellite*” after L. S. Ramsdell. In the tetragonal crystals, the oxygen atoms, lie in the same horizontal planes as the manganese atoms and grouped in pairs about each manganese atom, the groups are arranged on a body-centered tetragonal lattice. This close and compact structure results in a relatively strong bonding between the oxygen and the manganese atoms. In pyrolusite of this form, minute crystals with such structure occur as composite parallel groupings. In the orthorhombic crystals, on the other hand, the molecules are grouped in loose bundles and they form outer shells. The bonding between the oxygen and the manganese atoms in this form of pyrolusite is relatively weaker, the extra oxygen being disengaged by minimal external stimulation such as the low voltage current in a cell. A complex crystalline structure containing irregular intergrowths of ramsdellite and smaller proportion of pyrolusite is called “*gamma type*” Manganese dioxide or pyrolusite in contrast to the “*beta*” type which is the name given to the tetragonal form of pyrolusite. The gamma type pyrolusite is characterized by, apart from the particular arrangement of the molecules, some structural disorders or lattice defects called “*De Wolff*” disorders. These include, inter alia, inclusion of H ions within the crystal lattice. These H ions (also called “*structural water*” or “*crystal water*”) play an important role in electrochemical reactivity of pyrolusite in a cell.
- (10) **Electrical conductivity:** Pyrolusite is a good conductor of electricity.
- (11) **Corrosion resistance:** Pyrolusite i.e., MnO_2 and manganese metal are resistant to corrosion.
- (12) **Chemical affinity:** Pyrolusite has an ability to combine with a number of elements to form various inorganic and organic compounds.
- (13) **Nutrient:** Manganese is a critically important element in the plant, animal and human bodies.

USES

Manganese ore may be used directly or it may be beneficiated and agglomerated to some intermediate product for both metallurgical and nonmetallurgical uses. About 95% of ore produced accounts for the metallurgical and only about 5% for the nonmetallurgical uses. Manganese is the fourth most widely consumed metal after iron, aluminium and copper. Not one tonne of steel can be produced without manganese and it has rightly been described as the back bone of steel. Besides, its ore or chemical compounds are used for a wide range of products. The uses of manganese ore can be grouped as follows:

- A. Beneficiation
- B. Agglomeration
- C. Metallurgical
 - (1) Manufacture of ferromanganese
 - (2) Manufacture of silicomanganese
 - (3) Manufacture of spiegeleisen
 - (4) Extraction of manganese metal

- (5) Stainless steel
- (6) Pig iron and steel manufacturing
- (7) Nonferrous metallurgy
- (8) Electrolytic zinc and zinc smelting
- (9) Metal plating
- (10) Metallization

D. Nonmetallurgical

- (1) Synthetic manganese dioxide (electrolytic manganese dioxide or EMD, and chemically activated manganese dioxide or CMD)
- (2) Dry battery cell
- (3) Agriculture
- (4) Cattle and poultry feed
- (5) Chemicals
- (6) Glass
- (7) Ceramics, bricks and potteries
- (8) Drying of vegetable oil, paint and varnish
- (9) Ferrites

E. Miscellaneous uses (components in welding flux and foundry castings, coloured cement, catalysis)

These uses are discussed as follows:

A. Beneficiation: Beneficiation of low grade manganese ore is essential for optimum utilization of natural resources. The grade can be low not just because of low percentage of manganese, but mainly because of presence of various deleterious constituents like Fe, Pb, Cu, Zn, Ag, As, S, P etc. Out of these constituents, the most important impurity, in the Indian context and for metallurgical use, is phosphorus, which occurs in the form of very fine grains of apatite intergrown in the crystals of manganese minerals. On the basis of phosphorus content, Indian manganese ores are classified as:

Low phosphorus 0.08% P max

Medium phosphorus (+) 0.08–0.15% P

High phosphorus (+) 0.15% P

The high-manganese ores of India are generally also high-phosphorus containing more than 0.15% P (sometimes as high as 0.35%).

Brazilian ores are beneficiated by scrubbing, screening and classification, jigging, spiraling and Dyna whirlpool technology. Russian plants employ log-washing, multistage screening and classification, jigging, rod-milling, flotation and wet high intensity magnetic separation technologies. In India, hand sorting and visual grading are widely practised to upgrade the ore; manual jigging, mechanical jigging, washing, screening and dry and wet magnetic separation are also done in some mines. Dry high intensity magnetic separation is employed specially for upgrading MnO_2 - content in manganese dioxide ore fines, and wet high intensity magnetic separation requiring 100 mesh sized fines is practised for dephosphorization.

But the problem arises when dephosphorization is to be achieved, because of similar flotation characteristics of manganese minerals and apatite. Combination of several techniques including

flotation using special reagents, wet and dry high intensity magnetic separation, reduction roasting, tabling, jigging etc. is employed to upgrade manganese content, reduce SiO_2 and Fe contents and bring down phosphorus content to below 0.15% level.

B. Agglomeration: Agglomeration techniques include sintering, briquetting and pelletizing. These techniques have been explained in the chapter on hematite. Manganese ore fines are generated in mines after the lumps (+10 mm) are sorted out. Also, beneficiation requires crushing and grinding of the ores to liberate the gangue minerals, and the concentrates are in the form of fines. Fines from all these sources are subjected to one or the other type of agglomeration depending on the grain size. Generally, grains of (–) 10 mm to (+) 2 mm size are sintered, those of (–) 2 mm to (+) 325 mesh size are briquetted, and those of predominantly (–) 325 mesh size are palletized. For sintering, manganese ore is mixed with 7-8% coke and the mixture is fused at the corners of grains. For briquetting and pelletizing, some bonding material like bentonite or sodium silicate or pozzolana is added.

C. Metallurgical :

- (1) **Ferromanganese:** Ferroalloys are added to steel melting shops either as de-oxidizers or de-sulphurizers or alloying additives. Ferromanganese serves all the three purposes. Normally, 9-15 kg of ferromanganese is needed per tonne of steel produced. Removal of dissolved oxygen from liquid steel is accomplished by manganese of the added ferromanganese that forms an oxide having greater stability than that of iron oxide under the conditions of temperature, pressure and composition of steel-making furnace, due to its greater affinity for oxygen in comparison to iron. Residual oxygen in refined steel reacts with carbon to form CO and CO_2 which, during solidification, gets entrapped in steel ingot to form blow-holes or pin hole porosity. It also forms oxides of other elements which get entrapped in steel as inclusions thus adversely affecting the quality of steel. Similarly, because of its strong affinity for sulphur, manganese prevents sulphur that may find its way into the pig iron from the blast furnace, from combining with iron, and instead forms manganese sulphide. Both the oxide and sulphide of manganese go into the slag in the steel melting shop.

After these reactions whatever surplus manganese remains, gets added to the steel, and by doing so, imparts strength and toughness to the latter, increases its elastic limit and tenacity, and the manganese metal raises the temperature to which it is safe to heat steel without reducing its strength. Also, it is easier to alloy manganese with steel because of its lower melting temperature (1244°C) than that of steel. Generally, it is customary for steel to contain 1.0–1.6% Mn (e.g. rail steel contains 0.9–1.3% Mn, high strength steel 1.3–1.6% Mn). Larger Mn-content (12–13%) makes the steel very hard and tough with a zone of hardened structure on it. Some common manganese steels are:

<i>Manganese steel</i>	<i>Compositions</i>	<i>Properties/Uses</i>
(1) 1.5% manganese steel	0.3% C; 1.6% Mn	Crank shafts, connecting rods, axles, high tensile bolts and studs.
(2) 1.5% manganese-molybdenum steel	0.35% C; 1.6% Mn; 0.25% Mo	Similar to above, but requiring higher tensile strength.
(3) 1.5% Mn non-shrink steel	0.9% C; 1.5% Mn	Uses requiring high degree of hardness and fine structure, such as taps for nonferrous metals, screw plugs, gauges, blanking press tools, broaches.

<i>Manganese steel</i>	<i>Compositions</i>	<i>Properties/Uses</i>
(4) Nitralloy steels	0.2-0.5% C; 0.35% Si; 0.65% Mn; 1.6% Cr; 1.1% Al; 0.2% Mo; balance nitrided steel	Surface-hardened steel which are machinable.
(5) Hadfield steel or austenitic manganese steel	C 0.92-1.4%; Mn 12-14%; small quantities of Cr (1.8-2.2%) or Mo (0.5-2.0%) or Ni (up to 4%) or a little Al may be made	High toughness and ductility with high work hardening capability and good abrasion resistance under impact; suitable in rails, earth-moving machinery, mining machinery including rock crushers, grinding mills, dredge buckets, power shovels, bucket teeth and pumps. Addition of Cr enhances resistance to atmospheric corrosion and abrasion, that of Mo improves the toughness and resistance to cracking of castings, that of Ni stabilizes the austenite, and that of Al improves the abrasion resistance by reducing the tendency of carbon to form carbides as well as preventing the formation of martensite during quenching or deformation.

Ferromanganese, and not manganese metal is added to steel, because, in nature manganese ores occur invariably associated with iron, and it is costly to extract metallic manganese from them. Moreover, while the manganese of the ferromanganese performs the functions of purification and improvement of the steel, the iron simply gets added to the molten iron. so, by taking advantage of the association of the two metals in nature, manganese is added in the form of ferromanganese which is less costly to manufacture, without incurring any unnecessary cost for separating the two.

Ferromanganese atomized to ultra-fine sized powder, is called “*atomized ferromanganese*”, which is used to perform de-oxidizing and alloying functions in different varieties of welding electrodes and hard-facing operations. *Atomization* is the process of dispersion of a molten metal into small particles by a rapidly moving stream of gas or liquid (for more details see “Iron powder” in the chapter on hematite).

Ferromanganese may be of four types as follows:

- (i) *Standard or high carbon ferromanganese (HC Fe-Mn)*: This is used for addition to steel melting shop for the usual functions of de-oxidation, de-sulphurization and alloying. It may contain 65-82% Mn, 6-8% C and 1.5% (max) Si, 0.05% (max) S and 0.4% (max) P with practically the entire balance accounted for by iron. The world market prefers high carbon ferromanganese with 78% (min) Mn, 7.5% (max) C, 1.2% (max) Si and 0.2% (max) P. this grade of ferromanganese cannot be produced in India due to constraints of grade of ore. So, the Indian consumers accept the indigenously produced ferromanganese containing 70-75% Mn and 0.4% (max) P with carbon and silicon contents more or less at the same levels . The maximum Mn/Fe ratio in such ferromanganese can be about 5:1.

During the 1920s and 1930s or even earlier, ferromanganese was manufactured in shaft type blast furnaces. Now-a-days, the most common furnace employed is the electric arc furnace (EAF). The electrodes used are of graphite. Manganese ore, coke (reductant) and limestone/dolomite (flux) constitute the basic raw materials charge. The heat is provided by electric arc. The operation is power-intensive, the requirement of power being 2600-2900 kwh per tonne of ferromanganese smelted. During smelting, the oxides of Mn, Fe and Si along with some of the phosphorus is reduced to the element form in molten state and forms a solid solution. A part of the Mn oxide (up to 35% MnO equivalent to 27% Mn), Si and the oxides of Ca and Al combine together to form slag. While practically 100% of the iron of the ore is recovered, the recovery of manganese does not exceed 80-83 per cent.

Now-a-days, much attention is being focused on the use of “*plasma smelting*” and “*Kawasaki process*”. In the plasma smelting process, the heat is produced by plasma torches. Its advantage lies in its ability to use low grade ore fines and noncoking coal, but its main disadvantage is the high requirement of electricity. Although, this process is in use in Sweden for ferrochrome production, its application in ferromanganese production is in developmental stage. In the early 1980s, Kawasaki Steel Corporation, Japan developed a process on pilot plant scale, using a specially designed blast furnace consisting of an upper pre-reduction chamber and a lower smelting chamber, to smelt ore fines. But its commercial practice has not been known.

- (ii) *Medium carbon ferromanganese*: This is used for making low carbon steel. It contains 74–80% Mn, 1–3% C, 1.5% (max) Si, 0.05% (max) S and 0.4% (max) P. It is manufactured by refining high carbon ferromanganese and reducing carbon through silicothermic route using silicon as the reductant.
 - (iii) *Low carbon ferromanganese*: This is used for manufacturing chrome nickel steel (in which the carbon content is required to be at a level below 0.1%) and also very low carbon steel. It may contain 80–90% Mn, 0.07–0.75% C, 1–7% Si, 0.05% (max) S and 0.25% (max) P. As in the case of medium carbon ferromanganese, for low carbon ferromanganese also, the starting material is high carbon ferromanganese, which is refined by silicothermic process to reduce carbon content.
 - (iv) *Extra low carbon ferromanganese*: It is practically free from carbon, and can be manufactured by aluminothermic process involving smelting of the oxide with aluminium powder. it is used for some special types of steel.
- (2) **Silicomanganese**: Compared to ferromanganese, Silicomanganese is a very recent product developed on commercial scale for the first time in India during the late 1980s. Its development was prompted by the progressive deterioration every year of the quality of manganese ore produced in India. The percentage of manganese decreasing from 47–48 to 44–46 and that of silica increasing from 5–5.5 to 7–8. The Silicomanganese technology was developed as a substitute of ferromanganese, out of the sheer necessity to adjust to the changed resource availability of low-manganese high-silica ore. In this product, both manganese and iron are less and silicon is more compared to medium carbon ferromanganese. Its composition as per Bureau of Indian Standards (BIS) should be 50–74% Mn, 14–28% Si, 2.5% (max) C, 0.3% (max) P and 0.05% (max) S. In India, grades containing 55–65% Mn, 16–28% Si, 0.05–4.0% C, up to 0.35% P and up to 0.08% S are actually produced.

Silicomanganese also acts as a de-oxidizer and de-sulphurizer in steel melting shop, and in addition, it helps form manganese - and silicon-bearing alloys of steel. On an average, its consumption is of the order of 10 kg per tonne of steel produced. Sometimes, it may be used only for de-oxidation and de-sulphurization purpose, and then its consumption is 5-6 kg per tonne of steel produced. It is also manufactured in EAF like ferromanganese, but with a different grade of ore, and it is more power intensive than ferromanganese, the requirement of power being 3800-4200 kwh per tonne of ferrosilicon produced. A typical type of steel containing both silicon and manganese is Ferro-silico-calcium-manganese (Fe-Si-Ca-Mn) alloy containing 15% Mn and varying percentages of Si.

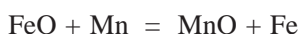
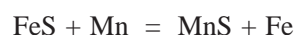
- (3) **Spiegeleisen:** It is sometimes referred to as “*silico spiegeleisen*”. The name is derived from the German words “spiegel” meaning mirror, and “eisen” meaning iron. Historically, this alloy of iron and manganese containing 15% Mn was the standard form in which manganese used to be traded till ferromanganese became popular. Now-a-days, it is sometimes used as a substitute of ferromanganese, out of the sheer necessity to adjust to the changed resource availability of low grade manganese ore containing high iron and high-silica. Spiegeleisen may contain 5-30% Mn, but the composition of a standard product is: Mn 20–22%; Fe 65%; Si 11 per cent.
- (4) **Manganese metal extraction:** Metallic manganese is used in alloys where iron is undesirable (e.g. manganese-bronze, Cu-Ni-Mn). It is also used as a de-oxidizer in nonferrous metallurgy. It can be produced by smelting reduction of the oxide of manganese by means of silicon or through the relatively costly aluminothermic route. But more commonly, it is extracted in electrolytic arc furnaces by electrolysis of $MnSO_4$ which is leached from low grade ore. The grades of metallic manganese vary as follows:

Mn	94.0 to 99.9%
Si	0.01 or less up to 1.0%
Fe	0.001 or less up to 2.5%
C	0.006 or less up to 0.2%
S	0.03 or less up to 0.05%
P	Trace to 0.1%
Al	Up to 0.5%
Heavy metals	Up to 0.005%
H ₂	Up to 0.015%
N ₂	Up to 6%

Manganese metal is used as an additive for making high quality steel and nonferrous metals.

- (5) **Stainless steel:** Standard products of nickel-chromium stainless steel are corrosion resistant hard and strong, and they contain 18–25% Ni. For making ordinary appliances, low-nickel (less than 5% Ni) stainless steel is used with relatively cheaper manganese substituting a substantial portion of the costly nickel, the strength and hardness of the product being provided by manganese.

- (6) **Pig iron and steel manufacturing:** In these, the role of manganese ore is mainly as de-sulphurizer and also as de-oxidizer. For pig iron manufacturing manganese ore (psilomelane, rhodochrosite) is used; but for steel-making, although ferromanganese is preferred, manganese ore can also be directly used if the purpose is only de-oxidation and de-sulphurization, and not alloying. The reactions, in essence, are:



It has been found that the velocity of removal of sulphur is also accelerated by a high CaO/FeO ratio. So, as more and more FeO is de-oxidized, the percentage of FeO in the melt decreases, resulting in an increase in the CaO/FeO ratio, which in its turn accelerates de-sulphurization. In other words, the process of de-sulphurization by manganese becomes more efficient due to its being at the same time an effective de-oxidizer.

- (7) **Nonferrous metallurgy:** In this, iron is undesirable. So, for the purpose of de-oxidation, de-sulphurization and alloying addition, manganese metal has to be used instead of ferromanganese. As an alloying additive, manganese improves strength and hardness of nonferrous metals. Some common alloys of manganese with nonferrous metals are:

<i>Alloy</i>	<i>Composition</i>	<i>Uses/Properties</i>
Manganese-copper	Mn 4–5%	Turbine blades
Manganese-bronze	Mn 3–4%	High grade brass used in ship propellers, fittings, gears and bearings, and in chemical and brewing industries.
Manganese-copper-nickel	Mn 8–12%, Ni 4%	Wires for electrical resistance, spark plug points, bimetallic strips for temperature control.
Manganese-aluminium	Mn 0.5-3.0%	Manufacture of aircraft tanks, beverage cans, food handling equipment, corrugated roofing sheets, bus bodies, colliery cage, paneling, car radiators, kitchen ware etc.
Manganese-aluminium-copper-magnesium	Mn 5%, Cu 4%, Mg 0.5%	Aircraft.
Manifor alloy	Mn, Cu, Mg, and Ni	Watch parts.
High-duty aluminium bronze	Cu 79.5% ; Al 9.5%; Fe 4.5%; Ni 5.5%; Mn 1%	Superior corrosion resistance in marine conditions; also high wear resistance.

<i>Alloy</i>	<i>Composition</i>	<i>Uses/Properties</i>
High tensile brass	Cu 55%; Zn 38%; Al 2%; Fe 2%; Mn 3%	Used where high-strength castings are required, as in marine propellers.
Manganin	Cu 80–86%; Mn 12–18%; Ni 1.5–2%	It has high electrical resistance and its thermal electromotive force (EMF) against copper is practically nil. It is used in precision electrical instruments like potentiometers, resistance boxes etc. and also in heating coils and electrical furnaces.

- (8) **Zinc metallurgy:** In this case of nonferrous metallurgy, the role of manganese ore is not de-oxidation, but oxidation. In electrolytic zinc refining process, zinc sulphate solution is used as the electrolyte. This solution must be purified prior to electrolysis. Iron occurring as ferrous sulphate solution mixed with zinc sulphate, is particularly objectionable. Pyrolusite *i.e.*, MnO_2 is used for oxidizing ferrous sulphate to ferric sulphate which precipitates and is filtered out. In the electrolytic refining operation stage, MnO_2 is used for coating lead anodes to prevent corrosion, and aluminium cathodes to facilitate stripping of the zinc deposits.
- (9) **Metal plating:** For electro-plating surface of a non-conducting material with metals like tin, palladium etc, it becomes necessary to pre-treat the surface with some absorbing metal oxide. Pyrolusite powder provides one such oxide *i.e.*, MnO_2 .
- (10) **Metallization:** Manganese is used to metallize surfaces to make them corrosion-resistant. Metallization is the process in which very small globules of a liquid metal are blown by a spray gun and sprayed on other metal surfaces to improve corrosion or wear resistance. The surface to be sprayed is first roughened by rough - machining or rough-grinding. The molten globules of metal, on being sprayed, immediately solidify and interlock by flattening.

D. Nonmetallurgical:

- (1) **Synthetic manganese dioxide:** This may be of two types namely, (i) *electrolytic manganese dioxide or EMD*, and (ii) *chemically activated manganese dioxide or CMD*. EMD is a high grade depolarizer in cells, albeit costly. On the other hand CMD is less efficient as a depolarizer and does not exhibit energy or power densities comparable to those of EMD.

The technology for manufacturing EMD has been developed during the late 1980s. The beta varieties of tetragonal crystalline pyrolusite (MnO_2) and the cryptomelane as commonly mined in India, are ground to fine size, reduced to MnO , which is then treated with H_2SO_4 acid to obtain $MnSO_4$. A high purity aqueous solution containing H_2SO_4 (20–60 grams per liter) and $MnSO_4$ (5–50 grams Mn per liter) is heated to 95–98°C, and then electrolyzed to get EMD deposited on the anode. Chemically, EMD is also MnO_2 , but the orthorhombic crystalline modification ramsdellite of gamma variety. EMD is capable of achieving high voltages, low polarization, high discharge capacities and long cell life.

For manufacturing CMD, manganese nitrate is first reduced at 600°C, and then quenched with 8–10% HNO₃ acid to get MnO₂ of the gamma variety. Alternatively, pyrolusite is roasted to 1050°C to obtain Mn₂O₄, which is treated with HCl.

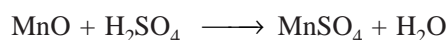
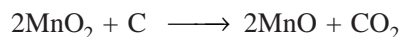
- (2) **Dry battery cell:** Either natural MnO₂ ore or synthetic MnO₂ (EMD or CMD) or a blend of the two is used as a depolarizer in dry cells. Cells may be of two types – primary (e.g. Leclanche cell) and secondary (e.g. lithium cell). The primary cells are discharged to exhaustion only once, while the secondary cells can be discharged and recharged multiple times. Now-a-days, high performance rechargeable cells are required in laptops, video cameras, cell phones etc.

In Leclanche type primary cells, carbon rod is dipped into an electrolyte (e.g. NH₄Cl, HCl) contained in a zinc container. Carbon serves as the anode and zinc wall of the container as the cathode. As zinc dissolves in NH₄Cl producing ZnCl₂, a difference in charge between C and Zn is produced causing electric current to flow. This chemical reaction also liberates hydrogen gas which goes towards carbon anode and accumulates around it. This is called polarization. The cover of hydrogen film on the anode causes resistance to the flow of current, and consequently decreases the efficiency of the battery. MnO₂ (mixed with graphite which is an excellent electrical conductor) serves as a depolarizer. This mixture is put in a linen bag, and the carbon anode rod is enclosed by it. The hydrogen ion, while passing through this MnO₂, combines with the oxygen and harmless Mn-hydroxide is formed, leaving the anode free from any deposition of hydrogen. If gamma variety MnO₂ is used, then the liberated hydrogen ions combine with the hydrogen ion residing within the crystal lattice of the MnO₂ and the oxygen to form Mn-hydroxide more quickly and efficiently. In India, common cells contain 25 grams of MnO₂ in which EMD accounts for 5 grams and natural MnO₂ 20 grams. In imported cells, EMD constitutes entire 25 grams. In pencil torch cells, the total MnO₂-content is 5 grams – all EMD.

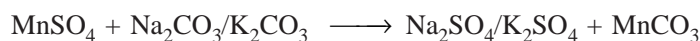
In rechargeable lithium cells, the anode comprises lithium metal or an alloy of lithium and aluminium (I% max) and the cathode is made up of either EMD, lithiated MnO₂ etc. with lithium salts dissolved in organic solvents as the electrolyte. During discharge, the liberated hydrogen ion gets into the crystal lattice of the MnO₂ and reduces it to Mn-hydroxide. During recharge, the hydrogen ion gets out to oxidize the Mn-hydroxide back to MnO₂.

- (3) **Agriculture:** Manganese is an essential trace element in the human body, its presence being in the range of 20-25 mg. The average global human ingestion of manganese is about 5-6 mg (maximum of 8 mg in Europe and a minimum of about 2-3 mg in USA, Japan and Australia). Human beings get their manganese from the food they ingest, and the route to the food is through the fertilizers that are added to the soil. The monoxide and sulphate of manganese are added to manganese-deficient soil along with the fertilizers in the form of micro-nutrient additives. Plants take up the manganese by osmosis. Manganese catalyses photosynthesis. Almost all cereals, pulses, fruits and vegetables, contain small quantities of manganese in them, which eventually find its way into the human body. Both the monoxide and sulphate of manganese are soluble in water and are applied to neutral and alkaline soils to help plants fight chlorosis and regain greenness and growth. The sulphate is particularly beneficial for tomato, potato, beans and maize. Manganese monoxide contributes to ossification, metabolism and the integrity of cellular membrane in human bodies.

The raw material to start with is pyrolusite. This ore is separated from iron, and then roasted with coke in an oxygen-depleted atmosphere in a reactor. The dioxide gets reduced to monoxide. By reacting the monoxide with sulphuric acid, manganese sulphate is obtained. The reactions involved are:

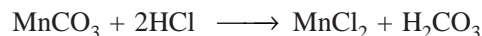


- (4) **Animal and poultry feed:** Manganese monoxide and manganese carbonate are used to supplement animal and poultry food stuff. The monoxide contributes to ossification, metabolism and the integrity of the cellular membrane in animal bodies. The process for producing monoxide and manganese sulphate from pyrolusite has been described above. The sulphate is reacted with sodium or potassium carbonate to yield manganese carbonate. The reaction involved is:



- (5) **Chemicals:** MnO_2 is used to manufacture different chemicals (in addition to the monoxide and sulphate described above) by digesting its powder in acids and other chemicals. The important ones amongst such manganese-based chemicals are as follows:

- (a) *Potassium permanganate:* Its composition is KMnO_4 . It is used as a powerful oxidizing agent for some chemicals, for treatment of municipal sewerage water, for odour control, for pollution control, in sugar refining, as disinfectants (algicide, bactericide, fungicide) etc.
- (b) *Hydroquinone:* It is used to make photographic developers, as a colouring agent and in medicines. It is also called *quinol benzene*, and its composition is $(\text{C}_6\text{H}_4(\text{OH})_2)$.
- (c) *Organic compound:* MnO_2 is used for making oxybenzoid by oxidation of di-benzanthronyl. It is also used for making various other organic compounds like naphthenate, borate, resinate, linoleate and oxalate which are used for drying vegetable oil, paints and varnishes. Other important organic compounds are manganese-ethylene-bisdithiocarbonate (used as agricultural fungicide) and methylcyclo-pentadienyl manganese carbonyl ($\text{C}_4\text{H}_6\text{N}_2\text{S}_4\text{Mn}$, used as an anti-knock in gasoline).
- (d) *Manganese sulphide:* Manganese sulphide or MnS_2 is used in calico printing, in leather industry, in match industries and in photography.
- (e) *Manganese chloride:* MnCl_2 is used in cotton textile as bronze dye, for giving a brown to black surface colour to bricks and as flux in magnesium production. It is produced by treating manganese carbonate (obtained from pyrolusite as described under (4) above) with hydrochloric acid as per the reaction:



- (f) *Manganese nitrate:* It is used as the base material for manufacturing chemically activated manganese dioxide.
- (g) *Manganese phosphate:* It is used as surface film on steel.

- (6) **Glass:** The raw material mixture for glass, namely silica, usually contains some iron, which forms ferrous silicate during glass-making. This ferrous silicate imparts a greenish tinge to the glass. The role of pyrolusite in glass is mainly to neutralize this greenish tainting effect, and also, by excess application, to impart amethyst colour to glass – specially ornamental glass.
- (7) **Ceramics, bricks and potteries:** The role of pyrolusite here is to impart red, brown, purple or black colour to the bodies and glazes. It is also used as an oxidizing agent to facilitate oxidation of some of the ingredients of the enamels at the time of fusion so as to give a speckled effect to the ceramic bodies.
- (8) **Drying of vegetable oil, paints and varnishes:** Oil, paints and varnishes dry by the uptake of oxygen. Various driers are added to them to accelerate this oxidation process. The exact mechanism by which driers act, is not known. But it is believed that they attract great amounts of oxygen, and this causes polymerization which results in thickening and drying. Since 19th century manganese-based driers are being used in oil, varnishes, artists' oil paint etc. In 1890, there was a reference of “*manganesed oil*” in art literature. Initially, manganese oxide was used, but later on manganese borate gained preference.
- (9) **Ferrites:** A detailed discussion on the ferrites may be seen in the chapter on hematite. Ferrites belong to a class of new generation ferro-magnetic ceramic materials. Manganese is an essential component in one of the most commonly used soft ferrites namely, manganese-zinc ferrites ($\text{MnO} \cdot \text{Fe}_2\text{O}_3$ 48%, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ 52%), finding applications for making transformers and inductors.

SPECIFICATIONS OF USE

In case of a natural commodity, the grade is hardly under the control of human beings. The specifications are dictated by the availability, processing technology and the sum total of the content of different constituents in all the raw materials that go into the process to get a desired output. Manganese ore is no exception. The grades specified and used by the industries depend on the interplay of all these factors. Nevertheless, certain principles underlying the specifications remain valid all the time. These are discussed with reference to some of the uses as follows:

A. Beneficiation: There is no particular specifications for manganese ores to be subjected to beneficiation. For hand sorting of lumps, a minimum size of 10 mm is required, because that is the size at which experienced human eyes can distinguish the different grades. So far as fines are concerned, the purpose of beneficiation is to increase the percentage of Mn and to decrease that of P, with economically viable recovery. All grades less than that suitable for direct use can be tried for beneficiation, but, in India, manganese ores containing Mn ranging from about 27–42% Mn and P as high as 0.35%, and dioxide ores containing 75% MnO_2 have been beneficiated.

B. Agglomeration: By application of just enough heat to fuse the corners of the ore particles, they are made to join together to form sinter. Very fine particles (size in microns) cannot be sintered as they will fuse altogether. Whatever cannot be hand sorted *i.e.*, (-) 10 mm, becomes a candidate for sintering. The size actually used by industries in India is (-) 6 mm to (+) 100 mesh.. Very fine sized particles of (-) 325 mesh (60%) are used to make pellets.

C. Metallurgical:

- (1) **Ferromanganese:** According to the Bureau of Indian Standards (BIS) the manganese ore to be used for manufacturing ferromanganese should contain: *Mn 38% to 48% and above;*

Fe 15% or less; Mn/Fe ratio varying from as low as 2.5 to as high as 7; SiO₂ 13% or less; Al₂O₃ 6% or less; SiO₂+ Al₂O₃ not more than 15%; and size 10-75 mm (85%). The principal constituents are manganese and iron, and the constituents like SiO₂, Al₂O₃, S, P, Zn, Cu, Barytes, CaO and MgO are considered deleterious. These are discussed as follows:

- (i) *Manganese and iron:* The grade of the ore to be used for manufacturing ferromanganese depends on
- the Mn/Fe ratio in the ferromanganese,
 - the recovery of Mn from the ore, and
 - the recovery of Fe from the ore.

The Mn/Fe ratio in the ferromanganese is dictated by the grade of the available ore, and it cannot be increased beyond a point. The last two factors depend on the status of technology at a given point of time and the operational efficiency of the plants. In India, the standard grade ferromanganese produced generally contain Mn and Fe in the ratio 75:16 ; the recovery of manganese is generally about 78-80%, and that of iron is 100 per cent. So, the Mn/Fe ratio can be worked out thus:

$$(\text{Mn/Fe})_{\text{ore}} = \frac{(\text{Mn/Fe})_{\text{alloy}}}{\frac{\text{Recovery of Mn}}{\text{Recovery of Fe}}} = \frac{75/16}{78/100} = 6$$

If now, any of the parameters – Mn/Fe ratio in alloy or the recoveries of the metals – changes, then the Mn/Fe ratio in the ore will also change accordingly.

But ferromanganese is valued primarily for its Mn-content, which is the de-oxidizer, de-sulphurizer and alloying additive. Iron gets into it by virtue of its natural association in the ore. So, besides Mn/Fe ratio, the Mn-content is important and it should be as high as possible, but again the best possible use has to be made of the locally available ore. Also, higher Mn-content means correspondingly lower Fe-content and vice-versa, and so the Mn-content and the Mn/Fe ratio are interrelated. The Indian industries generally get and use ores containing 38-40% Mn and 6-9% Fe, but some of them are known to have used ore containing as low as 30% Mn. The lower grade ores can also be used for blending with higher grade ores in the interest of making the best utilization of the locally available resources.

- (ii) *Silica and alumina:* Both SiO₂ and Al₂O₃ have higher melting point than manganese. So, they tend to increase the energy requirement for melting the charge, to decrease the fluidity of the slag and also to increase the volume of slag formation. Considerable portion of the available manganese pass into the slag, and an increased slag volume means it will draw more manganese into it, resulting in higher loss of metal. But, if all the raw materials together contain high phosphorus and sulphur, then slag plays an important role inasmuch as it absorbs these elements, and an optimum level of slag formation is desirable. So, both these constituents should be low, but not too low. In the Indian ores used for ferromanganese manufacturing, Al₂O₃ is not a problem, but SiO₂ is, and the industries are known to use ores with SiO₂ varying from as low as 1.5% to as high as 13 per cent.
- (iii) *Phosphorus and sulphur:* If, through the ferromanganese, phosphorus and sulphur are carried into the final product *i.e.*, steel, they reduce ductility and makes the steel

brittle under shocks, and the steel will be liable to crack at the time of rolling (see also chapter on hematite). Hence these impurities are highly objectionable. But it is also practically impossible to remove them beyond a point, because these elements are not completely absorbed by the slag, and remain distributed in the contact zone between molten metal and slag, and to remove them even partially, addition of extra flux (limestone) becomes necessary, which means increased fuel consumption and decreased productivity. Moreover, sulphur present in the ore will consume a part of the Mn to form MnS because of their mutual affinity, thus limiting the final availability of Mn for desulphurization of iron ore. So, phosphorus and sulphur in the manganese ore meant for ferromanganese production should be as low as possible, but again compromises have to be made due to constraints of local availability and beneficiation technology, and also the amounts of these elements coming from other raw materials count. As already discussed, in the high and medium carbon ferromanganese products maximum P-content is specified to be 0.4%, in the low carbon ferromanganese, it is 0.25%, and the maximum S-content in all types of ferromanganese is 0.05 per cent. So, the contents of these elements in the ore should be lower than these. The sulphur is not a problem in Indian ores, and the maximum limits of P-content in the ores actually used by Indian industries vary from 0.04-0.26 per cent.

- (iv) *Zinc*: Zinc, if carried into the furnace, escapes with the gas, condenses as ZnO after oxidation by the CO₂ and is deposited in the upper part of the furnace. If Zn-content is too high, then the heavy layers of ZnO formed on the inside walls of the furnace, the charging apparatus and the gas vents may cause operating problems. It should, therefore, be as low as possible.
- (v) *Copper*: Copper is sometimes desirable in some special steels for increasing resistance to atmospheric corrosion. But, generally, if copper content in steel is more than 0.3-0.4%, it begins to cause trouble in rolling or forging at high temperature. Copper forms a low-melting alloy on the surface of the steel that penetrates the grain boundaries and makes it difficult to obtain a surface free from minute cracks. Since this metal, if present in the manganese ore, is carried to the ferromanganese and finally to the steel, it is undesirable in the former.
- (vi) *Barytes, CaO and MgO*: Barytes (BaSO₄) releases sulphur. CaO is slag-forming material and creates problems in controlling the volume and characteristics of the slag in the furnace. MgO, like Al₂O₃, is refractory.
- (vii) *Moisture*: Manufacturing of ferromanganese is power-intensive and power is a costly input in India. On an average, for one tonne of ferromanganese, 2.5 tonnes of Mn-ore, 0.55 tonnes of coke and 0.3 tonnes of flux totaling 3.35 tonnes of raw materials are consumed. For every 1% increase in moisture, an additional 21 Kwh of power is required per tonne of ferromanganese. Indian industries endeavour to limit the moisture content in the whole raw material charge to 5 per cent to make their operations economically viable. As is the fact Indian coke contains up to 13% moisture in rainy season and about 7% moisture in dry season. So the moisture content in the manganese ore which constitutes the largest component (75%) in the raw materials has to be very low. Assuming the moisture content of the flux to be nil, its maximum limits in the manganese ore can be worked out thus:

(a) During rainy season:

$$[(5 \times 3.35) - (13 \times 0.55) - (0 \times 0.3)] \div 2.5 = 3.84\%$$

(b) During dry season:

$$[5 \times 3.35) - (7 \times 0.55) - (0 \times 0.3)] \div 2.5 = 5.16\%$$

If the flux also contains some moisture, then that in the manganese ore has to be still lower.

(viii) *Size:* Fine-sized ore hinders its thorough reaction with coke and flux in the furnace. If blast furnace is used, then fine ore particles will tend to choke the passage of air blast, and in case of electric arc furnace, the generation of electric arc will be adversely affected. It is necessary that there are air spaces within the charge and at the same time enough surface area is available for the reactions to be thorough. So, either lumpy natural ore or sinter or pellet or their mixture is used. The Bureau of Indian Standards (BIS) has in 1982 specified that at least 85% of the ore particles should be of 10–75 mm size. But in India, industries actually accept sizes ranging from (+) 5 mm up to even 100 mm.

- (2) **Silicomanganese:** Manganese ore containing lower percentage of Mn down to 35% and correspondingly higher percentage of SiO₂ compared to that required for ferromanganese is acceptable, as the product itself contains relatively less Mn and more Si. Since the furnace and the technology are similar to those deployed for ferromanganese manufacturing, the limitations with regard to the impurities and size of the ore for Silicomanganese are the same as for ferromanganese. In India, industries actually use 6–75 mm (generally around 35 mm) sized ore containing 35–40% Mn, 18–30% SiO₂, up to 22% Fe and up to 0.3% P. Silicomanganese is more power-intensive than ferromanganese. So, for the same reasons applicable in case of ferromanganese, the moisture content of the ore should be very low.
- (3) **Spiegeleisen:** Its production is not reported in India. But since the product is low grade ferromanganese, low grade ore containing relatively lower Mn and higher Fe can be used.
- (4) **Manganese metal and stainless steel:** For extraction of metallic manganese, the starting raw material is not manganese ore directly, but very high purity MnSO₄. Manganese ore is only required for making this chemical *i.e.*, MnSO₄. So, the grade of the ore is as for chemicals discussed later. In low-cost stainless steel manufacturing, manganese metal is used as an alloying additive in partial or complete replacement of nickel with a view to reducing the cost of production.
- (5) **Pig iron and steel:** The role of manganese in pig iron manufacturing in blast furnace is to de-oxidize and de-sulphurize, and not as an alloying additive. So, it is added in the form of ore directly instead of costly ferromanganese. If the purpose of its use in steel melting shop is limited only to these, then also the ore is preferred; but now-a-days in modern steel plants, it has become an established practice to use ferromanganese in order to produce high quality steel. For iron-making also, the consumption is now very small due to change of technology from blast furnace to basic oxygen furnace to electric arc furnace, having declined from an average of 70 kg per tonne of iron in the 1960s to 30 kg in the 1990s. The specifications are discussed as follows:

Type of ore: When ore is directly used, the type of ore is important. Since pyrolusite has extra oxygen in it and it acts rather as an oxidizer than as a de-oxidizer, it is not suitable. Ores like psilomelane, braunite, rhodochrosite are suitable.

Size: Manganese ore fines (like the fines of other raw materials namely iron ore, limestone, and coke) will tend to choke the furnace and obstruct smooth passage of air blast and completion of the reactions. So compact lumpy ore is specified. Blast furnaces are taller than steel melting shops, and consequently the ore has to withstand greater stress during the downward descent of the charge in the former compared to the latter. So the ore to be used in a blast furnace is required to be stronger and larger sized than that to be used in a steel melting shop. The Bureau of Indian Standards (BIS) has in 1985 specified 25–40 mm (80%) and 10–40 mm (80%) size ranges for manganese ores to be used for making pig iron and steel respectively. Manganese ore is not used in steel melting shops by important steel plants in India, but that actually used in the blast furnaces is more or less consistent with this specification, a notable exception being Bhilai Steel Plant which uses ore varying in size from 25–85 mm.

Chemical composition: Manganese is the most desirable constituent and phosphorus the most objectionable one. But since manganese has a limited function to perform, a high grade is neither cost-effective nor necessary. Moreover, it is the total manganese getting added that is important for counteracting surplus oxygen and sulphur in the furnace, and this can always be increased by increasing the quantity of manganese ore in the charge if the oxygen- and sulphur-contents so dictate. Further, by virtue of the nature of the ores, lower manganese in the ore means correspondingly higher iron which is not objectionable when added to the pig iron, or the steel. The BIS has specified a minimum of 25% Mn for both pig iron and steel making. Manganese ore is not used in steel melting shops by important steel plants in India, but the content of manganese in the ore actually charged into the blast furnaces of different plants in India varies from 28–37% and that of iron from 15–23 per cent.

Alumina and silica are inconsequential when ore is used in blast furnace, because firstly the quantity of manganese ore in the charge is very small and the total quantities of alumina and silica in it is almost insignificant compared to that going into the furnace through the iron ore, and secondly whatever may go, is taken care of by the slag. The contents of Al_2O_3 and SiO_2 in the manganese ore actually used in Indian blast furnaces are in the ranges of 5–13% and 5–25% respectively.

But, phosphorus, even in very small quantities, adversely affects the quality of steel to which it is carried through the pig iron. It makes the steel brittle under shocks and the steel tends to crack at the time of rolling. Moreover it is impossible to remove it in the slag as it migrates towards the metal-slag boundary zone (see the chapter on hematite). This impurity is a formidable problem in Indian manganese ores. The BIS has specified limits of 0.18% and 0.35% in ores for use in steel melting shop and blast furnace respectively. Manganese ore is not used in steel melting shops by important steel plants in India, but the content of phosphorus in the ore actually charged into the blast furnaces of different plants in India varies up to 0.3 per cent.

- (6) **Nonferrous metallurgy:** In this case also manganese is used for its triple action – de-oxidation, de-sulphurization and alloying addition. But, unlike in ferrous metallurgy, here iron is the most objectionable constituent, as its presence degrades the quality of the nonferrous metals like copper. So pure manganese metal instead of any of the Fe-Mn alloys is used.

- (7) **Zinc:** In this case of electro-refining of zinc by electrolysis of zinc sulphate solution, the role of manganese is just opposite *i.e.*, oxidation. Iron present in the zinc sulphate in the form of ferrous sulphate is oxidized to insoluble ferric sulphate and filtered out. So, in the ore there should not only be maximum possible availability of oxygen, but also minimum iron (iron interferes with the reaction between MnO_2 and ferrous sulphate). Thus pyrolusite (MnO_2) becomes the ore for use in this case, and the MnO_2 -content should be as high as possible with iron as low as possible. In the Indian industries, pyrolusite containing 70-75% MnO_2 and 5% (max) Fe is used.

D. Nonmetallurgical:

- (1) **Synthetic manganese dioxide:** The objective here is to change the crystalline structure of natural manganese dioxide to gamma type so as to make it suitable for use in dry cells. The starting material for both EMD and CMD is MnO_2 which is converted to MnSO_4 by reacting with H_2SO_4 (in case of EMD) or to Mn_2O_4 (in case CMD). Obviously, pyrolusite is the ore specified and its MnO_2 -content should be as high as possible. In the manufacture of EMD, iron interferes with the reaction between MnO_2 and H_2SO_4 and is therefore considered deleterious. Manufacture of CMD is not known in India, and the Indian EMD industries actually use pyrolusite containing 65–82% MnO_2 and up to 10% Fe.
- (2) **Dry cell:** For long and efficient functioning of dry cells, 300 mesh sized manganese ore fines (either natural or in the form of synthetic dioxide *i.e.*, EMD or CMD or a mixture) has to perform its depolarizing role effectively. For this purpose, the specifications are with regard to the following six principal parameters:
- (i) availability of oxygen,
 - (ii) reactivity of the available oxygen,
 - (iii) existence of hydrogen ion in the crystal lattice,
 - (iv) absence of iron,
 - (v) absence of moisture, and
 - (vi) absence of metals electro-negative to zinc.

The rationales of the specifications are elaborated as follows:

- (i) *Availability of oxygen:* Depolarization is achieved by oxidation of the liberated hydrogen to form manganese hydroxide in primary cells, and so mere high manganese content is not enough, there must be extra oxygen available in the manganese ore. Thus, the dioxide ore or pyrolusite with a high MnO_2 -content is the ore suitable for this use (if natural ore is to be used, otherwise synthetic dioxide). According to the US National Stockpile Specification, the MnO_2 -content in the natural ore should be 75% (min). According to BIS specification of 1984, the minimum MnO_2 -contents of the natural ore, CMD and EMD should be 72%, 85% and 90% respectively. The ores used by the Indian industries contain 70-84% MnO_2 .
- (ii) *Reactivity of the available oxygen:* Mere high MnO_2 -content and large availability of oxygen, as is the case with tetragonal crystalline form pyrolusite, may only achieve a very slow depolarization and can at best be used in radio batteries with slow drainage current, and not in high drainage current batteries (e.g., flash light cell). For the latter type of cells, the available oxygen must also be highly reactive. This condition is fulfilled by the orthorhombic crystalline form of pyrolusite called ramsdellite, or the CMD or the EMD with relatively weak bonding between manganese and oxygen.

- (iii) *Hydrogen ion in the crystal lattice:* The liberated hydrogen ion, while passing through the depolarizer MnO_2 , combines with the oxygen to form harmless Mn-hydroxide, leaving the anode free from any deposition of hydrogen. This process becomes more quick and efficient, if there is hydrogen ion (also called crystal water) residing within the crystal lattice of the MnO_2 . This is possible if gamma variety pyrobuxite is used – either natural or CMD or EMD. In rechargeable secondary high performance cells like lithium cells used in lap tops, cell phones, emergency lights etc., the crystal water of the gamma type manganese dioxide proves to be useful in another way. There, the cathode comprises lithiated manganese dioxide, and for making this product, lithium ion is introduced into the crystal lattice in replacement of the hydrogen ion already residing in it.
- (iv) *Iron content:* Iron is soluble in the electrolyte (HCl) in the dry cell and degrades the quality of the latter. But the pyrolusite and the synthetic dioxides based on it, invariably contain some iron. So, it is not enough for the dioxide to contain only high MnO_2 , but the iron-content should also be as low as possible. The US National Stockpile specifies a maximum of 3% Fe, while the BIS has, in 1984, specified maximum of 7% and 0.1% Fe in natural ore and EMD respectively (there is no specification for CMD). The Indian industries prefer ores containing up to 2% Fe, though some of them accept even up to 6% Fe. The EMD produced in India contains 0.07% Fe — well within the BIS limit.
- (v) *Moisture content:* The process of depolarization entails reaction between MnO_2 and H to form Mn-hydroxide. Presence of water molecules in the MnO_2 will hinder that reaction. Moreover the water may get into the electrolyte and dilute it. The BIS has specified a maximum limit of 3% moisture in all the three forms of MnO_2 – ore, CMD and EMD, while the industries in India accept 1- 4% moisture.
- (vi) *Metals electro-negative to zinc:* If a strong electric current is passed through a chemical compound, its decomposition (or *electrolysis*) into elements or parts takes place. Atoms of some elements collect in the negative pole or cathode, and those elements are called “*electropositive*”, and those elements the atoms of which collect in the positive pole or anode, are called “*electronegative*”. In the ordinary dry cells, the zinc container is the anode. So amongst the elements electronegative to zinc which are insoluble in the electrolyte, increase the resistance of the electrolyte to current; and those which are soluble, diffuse and deposit on the zinc container producing electric couple. The elements electronegative to zinc include copper, nickel, cobalt, arsenic, lead and antimony, and their presence in the manganese ore is highly objectionable and should be as low as possible. The BIS has, in 1984, specified the maximum limits of three of these elements thus: Pb trace to 0.1%, Cu 0.002 to 0.2%, Ni 0.003 to 0.04 percent. The manganese ores used by Indian industries conform to these specifications.
- (3) *Agriculture, animal and poultry feed, and chemicals:* The valuable element is manganese and the basic material is MnO_2 , which is used as an oxidizing agent and which is processed to yield the various usable product. So, pyrolusite containing high MnO_2 is preferable. This automatically ensures high manganese and high oxygen contents. Depending on the product, the ores actually used by the industries contain 72–92% MnO_2 .

Iron and silica are the most common objectionable constituents. When the process requires the manganese ore to be digested with acid, iron occurring in the form of oxide dissolves in the acid and is carried into the end-product as an impurity. When the process requires the manganese ore to be roasted with coke (as in the case of preparation of manganese monoxide for animal and poultry feed), the iron oxide also gets reduced by the coke and remains in the product besides consuming a part of the coke. Silica is insoluble in acids, but its presence increases the grinding cost of the ore. Besides, its excess presence makes the animal and poultry food unpalatable. The US Stockpile specifies a maximum limit of 3% each for iron and silica, but the Indian industries accept up to 5 per cent.

There are some impurities which are poisonous if the product is used for animal and poultry feed or medicines like Potassium permanganate (KMnO_4). The examples are copper, arsenic, cobalt, sulphur. Presence of each of them should be minimal – of the order of 0.02–0.05% or even less.

For efficient digestion with acid or reduction roasting, fine sized particles are preferred. The size generally preferred by industries is 150 mesh. The roasting of MnO_2 to MnO is carried out in oxygen-depleted condition without any air blast, and there is no question of the fine-sized material choking the furnace.

- (4) **Glass:** The colour of MnO_2 is the key in its use in glass. So a very high grade pyrolusite containing high MnO_2 is specified. For ordinary glass, a minimum of 80% MnO_2 , and for special glass, 90% MnO_2 is specified by the industries.

The main raw material for glass, namely silica, generally contains some iron oxide, which forms ferrous silicate imparting a greenish tinge to the glass product, and one of the roles of MnO_2 is to neutralize that effect. So the pyrolusite itself should not contain iron. Though for low quality ordinary glasses, the industries accept manganese ore containing up to 10% Fe, for good quality and special glasses, maximum limits of iron specified by the industries vary from 0.5 to 0.8%, and that for optical glass is 0.008 per cent.

The constituents Al_2O_3 , CaO and MgO are by themselves not objectionable for glass-making. Al_2O_3 gets into the batch through the feldspar, CaO through the limestone and MgO through the dolomite. Al_2O_3 increases the melting point of the raw material mixture, but it also imparts to the glass resistance to impact, bending and thermal shock. CaO compensates for the bad effect of Al_2O_3 by decreasing the melting point of the batch. MgO is an essential component for making colourless sheet glass and also to enable the glass to be drawn into tubes. BaO is added for making some kinds of special glass. But all these constituents are carefully controlled and balanced depending on the type of glass. Their presence in the manganese ore creates difficulties in controlling and balancing the proportions in the batch. That is why the industries do not prefer manganese ore containing excess of these constituents. The Indian industries use ores containing Al_2O_3 , BaO , CaO and MgO up to 1.5%, 1.3%, 0.4% and 0.4% respectively.

Carbonaceous matter is objectionable because of its colouring effect.

Silica should not be objectionable as such, because it will only add to the raw materials of glass. But high silica will be at the cost of MnO_2 -content of the pyrolusite – the main constituent for which it is valued. Moreover, for glass-making, pyrolusite is ground to (–) 200 micron size, and silica will increase its grinding cost. The industries generally specify a maximum limit of 2.8% for silica.

- (5) **Ceramics:** As in the case of glass, the colour of MnO_2 is the key in its use in ceramic glazes. Beside, in ceramics, the manganese ore serves to oxidize and fuse the enamels. So, on both the counts i.e., the colouring effect and the availability of oxygen, MnO_2 is the principal material, and high grade pyrolusite is the specified ore. The Indian industries generally use pyrolusite containing 86-87% MnO_2 .

WASTE UTILIZATION

Ferromanganese and silicomanganese account for about 95% of the consumption of manganese ore, and so most of the wastes are generated in these industries. Possibilities of utilization of these wastes have been identified as follows:

- (1) **Slag:** Bricks for construction purposes are manufactured utilizing the granulated ferromanganese and silicomanganese slags. Ferromanganese slag is also utilized as a manganese-bearing feed in production of silicomanganese.
- (2) **Ferromanganese fines:** Such fines mixed with manganese ore fines are agglomerated to produce sinters, which are useful for manufacturing of high-carbon ferromanganese.
- (3) **Waste gases:** The gases emanating from smelting furnaces are gainfully utilized as a fuel for calcinations of limestone, pre-reduction of manganese ore, pre-heating of ladles. It may also be possible to utilize these gases, after cleaning, in ignition system of boiler and sintering plants thus replacing expensive furnace oil.

SUBSTITUTION

Manganese has no substitute so far as its metallurgical uses are concerned. But in nonmetallurgical uses there are some substitutes as follows.

- (1) **Glass:** For the purpose of neutralizing the colouring effect of ferrous sulphate, antimony and arsenic are also effective.
- (2) **Vegetable oil, paints and varnishes:** Manganese oxide darkens the vegetable oil, paints and varnishes being dried. So, some organic compounds like naphthenate, borate, resinate, linoleate and oxalate of manganese serve as substitutes of natural manganese ore in this application.

SECTION - 2

METALS

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BERYLLIUM

Beryllium is one of the light metals, being considerably lighter than aluminium and slightly heavier than magnesium. But, still, it is not clubbed with the trio of light metals namely aluminium, titanium and magnesium, because it is extremely rare and relatively costly with limited usage. Its incidence in the earth's crust is only 50 ppm. Occurrence of beryllium to the extent of 8000 ppm has been reported from some coal ash. But the only commercial source of beryllium is beryl [$3\text{BeO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$], which is more known as a precious stone. Beryl occurs in granite pegmatite, mica schist etc. Theoretically, beryl contains 14% of BeO (5% of the metal beryllium). But commercial grades contain 11-13% BeO, 17-19% Al_2O_3 , 64-70% SiO_2 , and 1-2% alkali metal oxides. Since beryl occurs as crystals distributed at random within the host rock, it is mined only as a byproduct of minerals like feldspar, mica, spodumene etc., and then hand sorted.

HISTORY

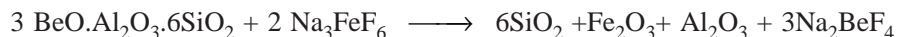
Two French scientists namely, Vanquelin (1797) and R.J. Haüy (1798), who found a new element in emerald, have been credited with the discovery of beryllium. Initially it was called "*glucinium*", due to the sweet taste of some of its salts. The name beryllium was given by a German scientist named F. Wohler, who first isolated the metal in 1828 by fusing beryllium chloride with potassium metal. But, since no use of it was known, no further interest was taken for a long time until in 1898, a French scientist named P. Lebeau succeeded in developing the electrolytic process and obtained over 99.5% pure metal from beryllium fluoride. By 1918 (*i.e.*, after World War-I), the process started being employed in USA for commercial production of the metal albeit in small scale. Although a process to make beryllium aluminium alloy was developed in 1916, the most important application of the metal namely, Be-Cu alloy, was developed in 1926. By the beginning of World War-II, *i.e.*, 1940, potentiality of beryllium for nuclear application was recognized. Since then both beryl and beryllium are considered as sensitive materials, and publishing of their production statistics has been prohibited in many countries including India.

RECOVERY

The starting material is finely ground beryl. Extraction of beryllium from it involves two steps – first recovery of BeO, and then that of the metal. Part of the BeO may be specially treated for some special uses like ceramics etc.

(1) **Recovery of BeO:** There are two processes – fluoride and sulphate.

(a) *Fluoride process:* In this process, the beryl powder is mixed with sodium fluoroferrate [Na_3FeF_6], briquetted and heated to 75°C yielding, inter alia, sodium beryllium fluoride [$3\text{Na}_2\text{BeF}_4$]. The reactions involved are:



The sodium beryllium fluoride, being water soluble, is separated from the rest by filtration. The filtrate is then treated with caustic soda [NaOH]. Beryllium hydroxide [$\text{Be}(\text{OH})_2$] is precipitated which, on firing at 800°C , decomposes to BeO.

(b) *Sulphate process:* First, the chemical reactivity of beryl with acid is improved by destroying its strongly developed natural crystal structure. For this purpose, the beryl is melted at 1625°C and suddenly quenched in water. Then, it is reacted with sulphuric acid to produce a solution of beryllium-aluminium-sulphate, to which ammonium hydroxide is added. From the resultant $\text{Be}(\text{OH})_2$ precipitate, BeO is obtained by firing. This BeO is impure, containing only 16–20% Be (cf. about 35% in pure BeO).

(2) **Metal recovery:** For this also, there are two processes as follows:

(a) *Thermal reduction:* The impure BeO is first treated with ammonium bifluoride to yield a solution of ammonium beryllium fluoride [$(\text{NH}_4)_2\text{BeF}_4$]. Then a series of treatments follow to remove different metallic impurities – with PbO_2 to remove manganese and chromium, with CaCO_3 to remove excess aluminium, and with aluminium polysulphide to remove the remaining heavy elements. Thus purified, the solution is evaporated and the residual [$(\text{NH}_4)_2\text{BeF}_4$] salt is heated to $900\text{--}1100^\circ\text{C}$ to decompose into ammonium fluoride [NH_4F] and beryllium fluoride [BeF_2]. On heating with magnesium metal at over 900°C , the BeF_2 is preferentially reduced to metallic beryllium.

(b) *Electrolysis:* First, the BeO is converted to BeCl_2 by passing chlorine gas over it in presence of carbon at 1000°C . BeCl_2 is collected as sublimate and is subjected to electrolysis at 730°C in a nickel or stainless steel cell (cathode) with graphite electrodes as anode. But the BeCl_2 being electrically nonconductor, is mixed with NaCl.

(3) **Ceramic grade BeO:** For making this, the impure $\text{Be}(\text{OH})_2$ obtained from sulphate process is treated with sulphuric acid or nitric acid or oxalic acid or acetic acid to yield corresponding salt (sulphate, nitrate, oxalate, acetate), which is decomposed to BeO at high temperature. If the temperature is $900\text{--}1000^\circ\text{C}$, then sinter grade BeO is produced, and if it is above 1000°C , then the product is refractory grade BeO.

CRITERIA OF USE

Beryllium has certain unique combination of properties not found in any other metal. The most important ones amongst them which make the metal indispensable in certain applications, are as follows:

(1) **Specific gravity:** Beryllium is very light. Its specific gravity is 1.85 (cf., 1.74 of magnesium and 2.7 of aluminium).

- (2) **Thermal properties:** Its melting point is relatively high—1284°C (cf., 651°C of magnesium and 660°C of aluminium). It is a good conductor of heat. But beryllium oxide is highly refractory.
- (3) **Mechanical properties:** It has high tensile strength (comparable with that of steel), and fatigue resistance, both together making it a strongly resilient metal with dimensional stability. But at the same time it is brittle.
- (4) **Corrosion resistance:** Resistance to oxidation is high. On exposure, like aluminium, it forms a thin film of oxide which prevents further oxidation. Beryllium is not readily attacked even by an extremely corrosive substance like liquid sodium metal.
- (5) **Electrical properties:** Compared to the well known conductive metals like silver, copper and aluminium, beryllium has somewhat low electrical conductivity – depending on purity, about 39 to 43% IACS (i.e., International Annealed Copper Standard).
- (6) **Nuclear properties:** It reflects neutrons, and in the process slows down their speed.
- (7) **Radioactivity:** There are several isotopes of beryllium, two out of which namely, Be^7 and Be^{10} are formed only in the upper atmosphere due to effect of cosmic rays, and are not useful. But another one namely, Be^{11} is highly radioactive having a very short half-life of only 14.1 seconds.
- (8) **Response to X-ray radiation:** X-rays are electromagnetic radiation of very short wave length (10^{-8} – 10^{-12} cm). Beryllium neither absorbs nor reflects X-rays, it transmits them with very low absorption. The measure of the rate of absorption of radiation is “*mass absorption coefficient*” which is the cross section area of the lost radiation for a given mass of the metal and is expressed in terms of area per unit mass (m^2/kg). For beryllium, this coefficient is the lowest amongst all metals.
- (9) **Magnetic property:** Beryllium is nonmagnetic.
- (10) **Toxicity:** Beryllium is highly toxic. Prolonged inhalation of its dust may produce a delayed disease of the lung called “*berylliosis*”. This toxicity is actually a negative criterion for wide usage of this metal, various safety measures adding to the costs.

USES

Beryllium, because of its scarcity, high cost and toxicity, is not used very widely or in large quantities. Hence, its use is generally in small quantities in combination with certain other metals – either as alloys or as intermetallic compounds, and in certain high-cost high-tech applications. Most of its present day uses are post World War-II (second half of 20th century) developments. The important uses are as follows:

1. Alloys
2. Intermetallic compounds
3. Nuclear reactor
 - (a) Fuel element
 - (b) Moderator
 - (c) Heat transfer unit
4. Source of neutron in laboratory experiments
5. Ceramics

- 6. Non-sparking tools
- 7. Chemicals
- 8. X-ray tube window.

1. Alloys: Beryllium has the ability to go into solid solution with a number of metals, the most important of which is copper.

(a) *Beryllium-copper alloys:* This was the oldest use of beryllium developed as early as in 1926. Beryllium and copper are in many ways complementary to each other, and consequently their alloys assume some unique characteristics. For example, beryllium is light and copper is relatively heavy; beryllium has high strength and high resilience combined with fatigue resistance, while copper is soft and malleable; and beryllium is only moderately electrical conductor, while conductivity of copper is very high. In addition, both the metals are nonmagnetic and good conductors of heat. Consequently, the applications of these alloys are in various objects requiring combination of these properties. Highly resilient current carrying springs, precision parts that undergo repetitive movements (e.g., camera shutters, delicate gears and bearings, critical parts of aircraft engines, etc.), inertial guidance instruments requiring light weight combined with high strength and high degree of dimensional stability are some of the examples.

The alloy is made not from beryllium metal, but from BeO. First, a master alloy is made by direct reduction of BeO with carbon and in presence of copper. This master alloy is then remelted and further amounts of copper and other metals added to obtain a desired alloy.

The important alloys of this group are:

<i>Beryllium content (%)</i>	<i>Copper content (%)</i>	<i>Other metals (%)</i>	<i>Properties/Uses</i>
1.6–2.85	96.8–98.4	Co : 0.065–0.35	5–6 times stronger than copper alone, also high fatigue resistance.
0.25–0.70	96.70–98.35	Co : 1.4–2.6	High electrical conductivity (60% that of copper alone), strong.

(b) *Other alloys:*

<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
High strength and high corrosion resistance alloy	60% Ni; 15% Cr; 7% Mo; 0.6% Be; balance Fe	Surgical instruments.
Surgical material	27% Co; 29.5% Cr; 36% Ni; 6% Mo; 1.5% Be	Excellent resistance to tarnish, and abrasion, compatibility with mouth tissues and body fluids, high strength, good casting properties, lower cost than precious metals. Used in dentistry and bone surgery.

<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
High resilience alloy	40% Co; 20% Cr; 15% Ni; 7% Mo 0.04% Be; balance Fe or 30% Ni; 8% W; 0.5% Be; balance Fe	Highly resilient, fatigue resistant, tarnish proof; suitable for watch spring.
High tensile strength alloy	98% Ni; 2% Be	Aircraft fuel pump, hypodermic needle, matrix for diamond drill bits.
Aluminium-beryllium alloy	0.1–0.5% Be; balance Al	Promotes fluidity of aluminium by refining the grains.

2. Intermetallic compounds: An intermetallic compound is different from an alloy inasmuch as the proportions of the component metals in the former is limited by their valencies, whereas there is no such limit in the latter. Beryllium forms intermetallic compounds with zirconium ($ZrBe_{13}$), niobium ($NbBe_{12}$), tantalum ($TaBe_{12}$) etc. These compounds are characterized by oxidation resistance even at temperatures above $1600^{\circ}C$, very high thermal conductivity and strength.

3. Nuclear reactor:

(a) *Fuel element:* In a nuclear reactor, the fuel element is a sort of container within which the fuel (e.g., an isotope of uranium) is placed. The requirements that have to be fulfilled are that (i) the fuel element must not absorb the neutrons released within the fuel due to fission (so that neutron economy of the fuel is maximized), (ii) it should not be damaged due to effects of radiation, and (iii) it should allow the heat generated due to nuclear fission to pass through for utilization in power generation. While magnesium is a suitable material for fabrication of fuel elements (due to its low neutron absorption along with its resistance to radiation damage and high thermal conductivity), it suffers from the disadvantage on account of its relatively low strength, and propensity for oxidation at high temperatures resulting in high inflammability. Even a very small addition of beryllium of the order of 0.005%, increases strength, retards oxidation and reduces inflammability. At the same time, beryllium does not limit the advantages of magnesium, because it reflects the neutrons back into the fuel, and also it is good thermal conductor. For this purpose, generally, magnesium is alloyed with beryllium or other metals in order to improve its strength.

(b) *Moderator:* As a result of fission within a fuel element, a fissile nucleus of the nuclear fuel breaks into a pair of unstable fragments, which undergo further radioactive decay until stable fission products are formed. But in the process some free neutrons are also released from the original nucleus, and these free neutrons become available for producing fission in more atoms. Under favourable conditions, this process may continue endlessly to produce what is known as chain fission or chain reaction, and hence, depending on requirement of power output, it becomes necessary to increase or decrease it with the help of some controlling device called

“moderator”. When introduced into the fuel, a moderator must have the ability to absorb neutrons in case of high energy neutrons (energies in the range of 1 million electron volts to 100 kilo-electron volts) or at least slow them down in case of low energy neutrons (energies of about 0.025 electron volt) so that the energy becomes too low to continue fission (the action is reversed when it is withdrawn). Beryllium does not absorb, but reflects neutrons, but in the process slows them down. So, it is suitable as a moderator in low energy system.

(c) *Heat transfer unit:* For transferring heat generated within fuel elements in a nuclear reactor, coolants are used. One of the coolant materials is liquid sodium metal, which is highly reactive. Beryllium is resistant to attack by it, and it is also good conductor of heat. However, in this application, if any oxygen is present in the liquid sodium metal – and it is difficult to obtain totally oxygen-free liquid sodium – it will form a thin film of beryllium oxide on the surface, which will inhibit transfer of heat. Calcium metal is therefore incorporated in the system. Calcium preferentially reacts with the oxygen and forms a stable oxide.

4. **Source of neutron in laboratory experiments:** For this purpose, beryllium-radium combination is used. Radium emits alpha particles which bombard the beryllium atoms. The latter break down with profuse emission of neutrons. Actually, experiments with this combination material led to discovery of neutron in the 1930s.
5. **Ceramics:** Both the sinter and refractory grades BeO recovered by processing commercial grade BeO, are used. The former is used for making electrically resistant porcelain, and the latter as a refractory in melting pots for very reactive metals. The latter is also used in high temperature units in nuclear reactors. Beryllia-silicon carbide (Be-SiC) ceramic composites find application as base to which silicon microcircuits are bonded. These composite material has thermal expansion close to that of silicon and hence stress developed due to high temperature is minimized; besides, it has high thermal conductivity and electrical resistivity.
6. **Non-sparking tools:** Sparks fly due to compressive force (in case of hammer) or shearing force (in case of cutting, drilling etc. tools). Part of the force causes particles from the surface of the tools to get dislodged while the remaining part is transformed to heat. Sparks are nothing but dislodged red hot surface particles, and they occur:
 - (i) if the surface is not strong enough to hold the particles under the force,
 - (ii) if the tool does not conduct heat quickly enough to prevent its accumulation on the surface particles.

Such tools which are prone to sparking, are not suitable in places containing explosive or inflammable substances, and non-sparking tools have to be used. Beryllium-copper alloy containing 2.25% Be is used in manufacturing non-sparking tools. Although a very good thermal conductor, copper alone is not suitable because it absorbs much of the force due to malleability and softening — more so due to the heat. Addition of beryllium adds strength to copper without significantly reducing its thermal conductivity (beryllium itself being a good conductor of heat), and its high melting point does not allow the surface particles to soften due to the heat.

7. **Chemicals:** Beryllium-based chemicals like its fluoride, acetate, hydroxide, carbonate, perchlorate, nitrate, bromide, carbonate etc. are used in ceramic preparation processes, in analytical chemistry and in organic synthesis. Zinc-beryllium silicate mixed with phosphorus is used for coating surfaces of fluorescent lamps, screens and signs.
8. **X-ray tube window:** Due to the strong ability of beryllium to transmit X-rays, it is used in windows of X-ray tubes. It is used in the form of an opaque piece of ultra-thin gauge foil or sheet. Besides allowing X-rays to pass through, it also serves the purpose of acting as a barrier between the external atmospheric conditions and the vacuum or inert gas environment inside the tube. Lead glass is also used, but beryllium is a better substitute due to its high strength and lightness.

CADMIUM

Cadmium is an extremely rare and hence expensive metal. Its incidence in the earth's crust is only 2 ppm. It is not found in nature independently, and is usually recovered as a byproduct from zinc smelters, and sometimes from copper and lead smelters also. It was discovered in 1817 by a German Scientist named F. Strohmeyer while analyzing zinc carbonate, and by J.C.H. Rology and K.S.L. Herman in zinc oxide.

Cadmium is a silvery white coloured, strong, malleable and ductile metal. It is a good electrical conductor. Its melting point is 320.9°C and boiling point 767°C. This low boiling point compared to that of lead (1620°C) and zinc (905°C) lends it amenable to recovery in vapour phase by fractional distillation. Cadmium has a high capacity to absorb neutrons. It is resistant to corrosion.

USES

- (1) **Alloys:** Low melting point of cadmium makes it suitable to form low melting alloys with lead, bismuth and tin. Such alloys can be used in fire detection apparatus and fire protection devices like automatic water sprinklers, safety fuses etc. (See also the chapter on bismuth).

Cadmium alloys very easily with copper. Addition of 0.7–1% cadmium to copper increases its strength and ductility and at the same time does not decrease the electrical conductivity significantly. This alloy is suitable for long-span overhead cables, and trolley wires.

Addition of cadmium to silver makes the latter resistant to tarnish due to corrosion, and this alloy is used in making silver ware. Cd-Ag alloy is also a good soldering material for special purposes. Alloy containing 98.65% cadmium and 1.35% nickel was used in high strength bearings during World War-II. Similarly an alloy containing 0.2–2.25% Ag, 0.25–2.0% Cu and balance Cd was also used for the same purpose.

The other important alloys are :

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Aluminium-cadmium-silicon	Cd in Al-Si matrix	Improved wear resistance and strength; used in highly loaded engine bearings.
Leaded aluminium alloys	8% Pb; 1% Cd; 1-4% Sn or Up to 10% Pb; 3-5% Cu; 0.5% Ni; 0.3-0.8% Mg or More than 10% Pb; small percentages of Cu, Mn, Zn, Fe and Si or More than 17.5% Pb	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.
Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu; Al-Si alloys containing 2-24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base	Used in self-lubricating bearings and other antifriction applications.
Aluminium-mica alloy	Mica coated with Ni or Cu with addition of Mg	Good solid lubricant; can be used in bearings.

- (2) **Electroplating:** Though cadmium plating renders iron or steel corrosion resistant, cadmium is very expensive so cadmium plated iron and steel articles are used for highly specialized and sophisticated purposes, such as aircraft parts, motor car fittings etc.
- (3) **Atomic reactor:** In a nuclear power plant, fuel element is a sort of container or matrix within which the fuel is placed. And the fuel elements are housed in a 'reactor'. Within a reactor, mechanisms are provided to regulate the generation of heat depending upon requirements, and for this purpose, control rods with ability to absorb neutrons are used. If the rods are lowered down in the reactor, more neutrons will be absorbed and the process of fission will slow down, thus reducing the heat. On the other hand, if the rods are pulled up out of the reactor, then less number of neutrons will be absorbed, and consequently process of fission will accelerate, thus increasing the heat. The neutron-absorbing capacity of pure cadmium metal makes it suitable for use as control rods in atomic reactors (See also chapters on beryllium and boron).
- (4) **Rechargeable battery:** A battery is a device that translates chemical energy into electricity. Rechargeable or secondary batteries contain active materials that are regenerated by charging, in contrast to primary ones in which the energy is exhausted as materials are consumed. Essentially, a battery contains a chemical and two electrodes. When it is used, chemicals near one of the electrodes begin a reaction that produces extra electrons, which constitute electric current. *Nickel-cadmium(Ni-Cd) batteries* have a

cadmium anode, a nickel oxyhydroxide cathode and an electrolyte of an aqueous solution of potassium hydroxide. Cadmium accounts for 13-15% of the weight of a typical cell. These have several advantages inasmuch as they can function at low temperatures and can be recharged at high currents, and they have long lives (over 3000 cycles of charge and discharge), minimum voltage drop and wide range of operating temperature (18-74°C). However, such batteries are very expensive and hence reserved for use for electronic devices for their long life and precision in delivery of current (e.g., shot duration switch tripping devices, engine starters, navigation systems, telecommunication back-up etc.). However, such batteries suffer from what is called “*memory effect*”. This means that if a cell is recharged before it is fully discharged, the remaining charge gets registered as the bottom line, and every time the cell will stop functioning at that level of charge.

- (5) **Pigments:** Cadmium salts serve as colouring agents for glass, enamels, paints, soap, rubber, paper, leather printing ink, textiles etc. The Sulphide is known as ‘cadmium yellow’, sulphoselenide as ‘cadmium red’.
- (6) **Photography:** The bromide, chloride and iodide of cadmium are sensitive to light and can be used in photographic films.
- (7) **Television picture tube:** Blue and green components of colour are due to cadmium phosphor in the colour picture tubes.

WASTE UTILIZATION

The principal waste is generated on account of the cadmium-nickel content of battery scrap (about 50% of the world’s production of cadmium is used in the manufacture of storage batteries). It has been reported that a new technology has been developed for extraction of cadmium from a complex solution through a series of upgradation process and finally electro-deposition. This technology has been claimed to have potential to recover cadmium from battery scraps.

CALCIUM

Calcium is an emerging alloy metal. It is isolated by electrolysis of molten CaCl_2 . Commercial calcium has 98% purity. It has strong affinity for both oxygen and nitrogen with which it forms CaO and Ca_2N respectively, at elevated temperature. But when exposed to oxygen at ordinary temperature, it forms only a thin film of oxide that prevents further oxidation. Its ability to form alloys with metals are more and more being evident. Its affinity for oxygen and nitrogen makes it a suitable agency for fixing oxygen and nitrogen respectively. In the form of CaO , it can be a carrier of nitrogen also, because CaO is stable and does not react with nitrogen. The currently important uses are as follows.

1. Alloys: Following is a list of some important alloys:

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Ferro-silico-calcium	30% Ca; 60% Si; 10% Fe.	Modification of inclusion for better mechanical properties in continuous casting of metals in which high silicon-content is desirable.
Calcium-iron	30% Ca; 70% Fe.	Modification of inclusion for better mechanical properties in continuous casting of metals in which silicon is not desirable.
Calcium-aluminium-iron	30% Ca; 25% Al; 45% Fe.	Deoxidation and modification of inclusion for better mechanical properties in continuous casting of metals in which high silicon-content is desirable.
Calcium alloy nitride	23% N; free C; 15% CaO ; balance Fe.	Carrier of nitrogen for nitrogenization purpose.

2. Nuclear reactor: For transferring heat generated within fuel elements in a nuclear reactor, coolants are used. One of the coolant materials is liquid sodium metal, which is highly reactive. However, in this application, if any oxygen is present in the liquid sodium metal –

and it is difficult to obtain totally oxygen-free liquid sodium – it will form a thin film of oxide on the surface of the metal container (e.g., beryllium), which will inhibit transfer of heat. Calcium metal is therefore incorporated in the system. Calcium preferentially reacts with the oxygen and forms a stable oxide.

3. **Lead-calcium battery:** This is an improved version of common rechargeable lead-acid battery. The plates are made of lead-calcium alloy instead of lead alone. These have low self-discharge as long as the weather is not too warm. Once charged, it remains so for months. In a further improvement, tin is added to the lead-calcium alloy and the electrolyte is captured in a fibre glass matter in the form of a gel. This type of battery is called '*absorbed electrolyte battery*', and is characterized by extremely low discharge rate.
4. **Vacuum tubes :** Calcium serves to de-gas vacuum tubes by fixing residual oxygen and nitrogen.
5. **Vanadium metal recovery:** To make elemental vanadium, vanadium pentoxide is mixed with calcium metal chips and ignited.
6. **Micronutrient:** Calcium builds bones and teeth, and helps maintain bone strength. Calcium is also used in muscle contraction, blood clotting and maintenance of cell membranes. Calcium is used in the preparation of vitamin-B and some food supplements.

CESIUM

Cesium, lithium, sodium, potassium and rubidium constitute what is called the 'alkali group' of metals. It was discovered in 1860 by R.Bunsel and G. Kirchnoff, and its name was derived from the same Latin word meaning sky-blue. The principal natural compound of caesium is pollucite (hydrated silicate of cesium with aluminium), which is of extremely rare occurrence. However, it may also be found albeit in low concentrations of less than 1%, in various minerals like lepidolite, beryl, microcline, feldspar etc.

CRITERIA OF USE

Cesium has two isotopes – Cs-137 and Cs-133. The Cs-137 isotope is radioactive and is the hazardous component in nuclear power plant wastes. It is the Cs-133 isotope (generally referred to as cesium only) which is used. But even this has to be used with extreme care because of its hazardous nature. It explodes violently when in contact with water, and its hydroxide is the powerful base that corrodes glass and eats into flesh. Prolonged exposure to cesium may produce a disease called '*cesiophiles*'.

The important practical uses of cesium are based on its property of high degree of photo-emissivity (see the chapter on 'Rubidium'), natural frequency of its atoms, and also its ability to remain liquid in a warm room (cf., mercury and gallium) and the ease with which it can be vaporized (more so under low pressure conditions or in vacuum).

USES

- (1) **Photoelectric cells and photometry:** The high sensitivity of cesium to variations in intensities of visible light is the principal criterion.
- (2) **Radio vacuum tubes:** High degree of photo-emissivity makes cesium useful in this application (See also chapter on 'Rubidium').
- (3) **Sniperscope and snooperscope:** These are invisible infrared viewing devices used during night by guards, military persons etc. for seeing objects as distant as 15 - 16 kms away. Infrared rays are transmitted from an infrared lamp source. These rays strike upon an object and are reflected back to a cesium surface. Cesium being highly photo-emissive, it emits electrons. These electrons are then directed to hit a fluorescent screen to produce a visible image of the object.

- (4) **Cesium clock:** For measuring extremely small time spans – even up to quintillionth of a second (10^{-18} seconds) — accurately, atomic clock is used. Atomic clocks are of two types – cesium clock and rubidium clock. Cesium clock consists of a tower constructed in a room insulated from humidity, and is stationary, while the rubidium clock is portable. Cesium clocks (also called cesium beam atomic clock) use the natural resonance frequency of Cs-133 atoms (9192631770 cycles per second), and are accurate to 1 second in 1 million years. This clock was invented in 1958, and the most well known clock was constructed in 1968 at the National Institute of Standards and Technology, Boulder, Colorado, USA, which is currently the standard reference for time in USA. Cesium clock has now made possible to redefine the unit of length ‘metre’ in terms of distance traveled by light in 0.000000003335640952 seconds. This is the same as per the historical definition, according to which a metre is equal to the length of a platinum bar kept securely in Paris, but at the same time, the new definition is more scientific and universally verifiable by anybody anywhere with the help of a cesium clock. These clocks can also measure the frequencies of pulsars.

To start the operation of a cesium clock, a stream of Cs-133 vapour is first introduced into a vacuum chamber. Then the atoms are concentrated into a ball at the centre by 6 laser beams, thus slowing down their oscillations so much that they cool down to a near absolute zero temperature (-273°C). Finally a single laser beam pushes the ball up a tower by one metre or so. On turning off the laser, the ball of atoms comes down due to gravity, triggering its natural frequency in resonance with microwaves, and this frequency is the basis of measuring time.

(5) **Other Uses:**

- (a) Infrared photography.
- (b) Television screens.
- (c) Television cameras.
- (d) Ship to ship infrared signaling in navy.
- (e) Catalyst in polymerization of organic compounds.

COBALT

Cobalt is somewhat sparse in nature, its incidence in the earth's crust being only about 25 ppm. The commercially important ores are heterogenite (oxidized ores, also known as black oxides, having composition $\text{CuO} \cdot \text{CoO} \cdot 3\text{Co}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$; mined in Congo and Zambia), linnaeite (Co_3S_4 ; mined in Russia, Canada and Australia), cobaltite or cobalt glance (CoAsS ; mined in Canada), Smaltite or speiss cobalt (CoAs_2 ; mined in Morocco), Erythrite or cobalt bloom ($\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$; mined in Morocco), carrolite (CuCo_2S_4 ; mined in USA), skutterudite (CoAs_3 ; mined in Morocco), asbolite (earthy variety of cobalt oxide occurring in nickeliferous laterite in New Caledonia, Cuba, Indonesia and Australia). But, except the sulphide ore of Zambia, cobalt is generally not found in sufficient quantities to be economically minable alone, and it is recovered mainly as byproduct of copper, zinc and nickel. Wastes and slags of old mines are also processed for recovering cobalt. A potential future source of cobalt may be the poly-metallic nodules of deep sea bed and the cobalt-rich (2.5% Co) encrustations of shallow ocean beds.

HISTORY

Cobalt compounds were in usage since historical times as a blue colouring agent without any knowledge about their chemical nature. They were used for colouring glass, porcelain, statuettes etc. during as far back as the Egyptian, Persian and Mesopotamian civilizations. But since those unknown compounds were poisonous, some time during 16th century, they started being called by the German word "*Kobold*" meaning goblin. The metal was first isolated in 1735 by a Swedish chemist called George Brandt, and subsequently, it came to be known by the name cobalt. Later on it was found that the poisonous effect of the compounds was not due to cobalt, but due to other elements like arsenic, present in the compounds.

In India, there were some irregular occurrences of a complex ore containing cobaltite and donaitite (iron sulpharsenide), locally known as "*sehta*", in Khetri area of Rajasthan. This ore was mined until 1908 for use as a blue glazing material in enamel works. Other occurrences of cobalt minerals in India, are not of any economic interest. Now there is no production of primary cobalt here, and production of some quantities of secondary cobalt are sometimes reported. The world production of the metal, which was about 6000 tonnes in 1948, reached the level of over 38000 tonnes in 2001.

RECOVERY

Extraction of cobalt depends on its original form, whether arsenide, oxide or sulphide. The low grade ores are concentrated by gravity, magnetic and flotation techniques. The metallurgical operations are as follows:

- (a) *Mixed copper-cobalt sulphides*: The ore containing cobalt, copper, iron and other metals, is smelted and reduced in electric arc furnace (EAF) to obtain two alloys – (i) a white alloy rich in cobalt (42–45%) and iron, but poor in copper (about 15%), and (ii) a red alloy rich in copper, but poor in cobalt (6–7%). The red alloy is treated in rotary furnace to obtain cobaltiferous slag which is returned to the EAF to produce white alloy. The white alloy is then dissolved in hot 20%-sulphuric acid. Copper does not go into solution and is separated, while the cobalt and iron are dissolved. Precipitation of cobalt in the form of hydrate is achieved by treating this solution first with sodium chlorate and soda ash, and then with sodium hypochlorite. Cobalt hydrate is slowly calcined to drive off part of oxygen and then is reduced by CO-gas, cooled and magnetically separated. The final product is 97-99% pure.
- (b) *Oxidized cobaltiferous copper ores*: These ores contain less than 0.5% Co. Such ores are electrolyzed in electrolytic copper plants, copper is recovered, and the cobalt oxide precipitate is again subjected to electrolysis along with a pulp containing cobalt hydrate powder in suspension. The cobalt deposited on cathode is refined in an EAF.
- (c) *Nickeliferous laterite*: The concentrate is smelted to yield a nickel-cobalt matte, which is crushed, leached with sulphuric acid, cobalt precipitated as hydrate as in the case of sulphide ore described under (a) above. Alternatively, the concentrate is subjected to hydrometallurgical method involving leaching with ammoniacal solutions under pressure.
- (d) *Arsenide ore*: The concentrates are roasted to remove the arsenic as As_2O_3 . Alternatively, they can be leached and cobalt precipitated with hydrogen as in the case of sulphide ore.
- (e) *Zinc extraction wastes*: The Hindustan Zinc Limited (HZL) in association with Bhabha Atomic Research Centre (BARC) developed and commercialized in 1994, a process for recovery of cobalt from its zinc smelting wastes called “beta cake”, which contained 1.0-1.5% Co along with varying amounts of iron, zinc, magnesium, copper, cadmium etc. The process comprised washing of the beta cake with acid and water to remove part of the magnesium and zinc contents, followed by roasting to remove the organic impurities, acid leaching, iron precipitation and finally solvent extraction and electro-winning of metallic cobalt. The most important step *i.e.*, the solvent extraction, is based on the relative affinity of various elements for the organic reagent di-ethyl-hexyl-phosphonic acid (DEHPA).

CRITERIA OF USE

Cobalt melts at 1495°C. It is a strong hard wear- and corrosion-resistant metal which retains these properties at high temperatures of even up to about 1000°C. It is ferromagnetic (ferromagnetic materials are either naturally magnetic or attracted to a magnetic field and may be easily magnetized due to their ability to concentrate the magnetic flux by a factor of more than 10 compared to vacuum). Natural cobalt is in the form of a stable isotope cobalt-59; but it absorbs neutrons and transforms to its isotope cobalt-60, which is radioactive with ability to emit strongly penetrative gamma rays (radioactivity is the spontaneous disintegration of certain heavy elements accompanied by the emission of high energy radiation, which consists of three kinds of rays: positively charged alpha particles, negatively charged beta particles and electromagnetic rays called “gamma rays”).

USES

The main uses of cobalt are in (1) alloys, (2) cutting tool, (3) permanent magnet, (4) sterilization and radiotherapy, (5) pigments and chemicals, (6) drying of paints, varnishes, ink etc., and (7) plant and animal nutrient. These are described as follows:

- Alloys:** The strength and the wear- and corrosion-resistance at high temperature makes cobalt a desirable component in some alloys for special usage. The examples of such alloys are:

<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
12% cobalt super high speed steel.	0.8% C; 4.5% Cr; 21.0% W; 1.25% V; 12.0% Co.	Heavy duty machining on high tensile alloy steel; forged products; close-grained cast iron products; railway coach tires, jet propulsion engines.
High temperature nickel-cobalt alloy	Ni and Co.	Not yet commercially produced. It has potentiality for use in hypersonic aircrafts.
Nimonic	58% Ni; 20% Cr; 17% Co; 2.5% Ti; 1.5% Al; 0.13% (max) C.	Creep resistant at temperatures up to 920°C; used in gas turbine blades and discs, hot-working tools.
Nimocast	76% Ni; 19% Cr; 0.3% Mn; 0.3% Cu; 0.4% Ti; 0.3% Al; 1.5% Co; 0.1% C.	Resists oxidation at temperatures up to 1100°C; it is a casting alloy.
Stellite	25–30% Cr; 1% (max) Mo; 2–15% W; 0.25–3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co.	Used in hard facing materials (e.g., armaments, cutting tools).
Super-alloy of steel	Up to 65% Co.	High temperature alloy capable of retaining its strength at temperatures up to 1150°C; required in gas turbines, jet engines.
Surgical material	27% Co; 29.5% Cr; 36% Ni; 6% Mo; 1.5% Be.	Excellent resistance to tarnish, and abrasion, compatibility with mouth tissues and body fluids, high strength, good casting properties, lower cost than precious metals. Used in dentistry and bone surgery.
High strength copper-cobalt-beryllium alloy	0.065–0.35% Co; 1.6–2.85% Be; balance Cu.	5–6 times stronger than copper alone.
Electrical copper-cobalt-beryllium alloy	1.4–2.6% Co; 0.25–0.60% Be; balance Cu.	Electrical conductivity 60% that of copper alone, and high strength.
High resilience alloy	40% Co; 20% Cr; 15% Ni; 7% Mo 0.04% Be; balance Fe.	Highly resilient, fatigue resistant, tarnish proof; suitable for watch spring.

2. **Cutting tools:** Cobalt is used as a binder in cemented tungsten carbide tools, which are produced by sintering (i.e., insipient fusion) a mixture of tungsten carbide and cobalt in dies of desired shapes. Such tools are highly wear-resistant (due to hardness and strength of cobalt) and resistant to softening at high temperature (due to high melting point of tungsten). Hence they are suitable for use under high temperature operating conditions, as in drilling bits.
3. **Permanent magnet:** Permanent or hard magnets, once magnetized, retain their magnetic field indefinitely even after the magnetizing field is withdrawn. Magnetic alloys made by powder methods have uniform flux density and fine grain structure. Due to its ferromagnetic property combined with strength at high temperature, cobalt is practically an indispensable component in making alloys for use as permanent magnets. It is a constituent in “alnico” — an alloy of cobalt (25%), aluminium (8%), nickel (14%) and iron (50%) with little copper, niobium, silicon and titanium, and in SmCo alloy (also called Co-rare earth alloy) made of samarium and cobalt, both of which are made by powder metallurgical techniques and used in permanent magnets. These magnetic alloy have uniform flux density and fine grain structure. The magnetic field strength of alnico is 1500 gauss i.e., 3000 times the earth’s magnetic field, and its curie point (i.e. the temperature above which a substance loses its magnetism) is the highest amongst all magnetic materials – 800⁰C. It is used in generators, motors, communication/acoustic equipment etc. The SmCo magnet, though costly in comparison to alnico, is valued for its small volume and high efficiency. It has the highest magnetic property amongst all known materials. (see also the chapter on rare earth metals).
4. **Sterilization and radiotherapy:** The property of radioactivity – more particularly the ability to emit gamma rays, is the key to this application. Gamma rays are harmful to life, but if suitably regulated, they can kill germs as well as create conditions in which germs cannot thrive for a considerable length of time even after withdrawal of the rays. When cobalt is inserted into nuclear reactors, it absorbs neutrons and transforms into cobalt-60. This cobalt-60 has the ability to emit gamma rays fast, and can be conveniently used for the purpose of sterilization and radiotherapy. Items of food, seeds, surgical instruments may be sterilized by exposing them to gamma rays emitted by cobalt-60. In the same way, harmful microbes in diseased body cells can be controlled through radiotherapy.
5. **Pigments and chemicals:** Cobalt compounds have traditionally been used as pigments for colouring enamel, glass etc. The common pigments are: cobalt green (CoO.ZnO), cobalt purple (cobalt acetate), different shades of cobalt red (cobalt carbonate, cobalt sulphate), different shades of cobalt blue (cobalt chloride, cobalt aluminate), cobalt black (cobalt oxide), turquoise green (cobalt titanate). The chemical cobalt chloride is also used as a mordant in dry cleaning.
6. **Drying:** Oil, paints and varnishes dry by the uptake of oxygen. The exact mechanism by which the drying takes place, is not known. But it is believed that the unsaturated fatty acids in oils make them reactive and they attract great amounts of oxygen causing polymerization. This ability of unsaturated oils make them form a solid, coherent and adherent film when spread on a surface and exposed to air. Normally, this process of oxidative polymerization is slow taking 12-36 hours. Various driers called siccatives, are, therefore, added to them to accelerate this process. Compounds of cobalt with long fatty acids called “cobalt soaps” (e.g., cobalt naphthenates, cobalt carboxylates) are the most widely used paint driers. Their performance is the best at ambient temperature.

- 7. Nutrient for plants, animals and humans:** The vitamin B-12 is the only vitamin containing cobalt as a trace element in the centre of its molecular structure. It is because of this that the chemical name of B-12 is “*cobalamin*”. Humans and all vertebrates as well as plants require cobalt which is assimilated only in the form of B-12, and the natural B-12 is synthesized by bacteria only if cobalt is available to them.

Cobalt is important for survival and growth of plants. Bacteria in root nodules of legumes require cobalt to synthesize B-12 and fix nitrogen from air – a process necessary for maintaining nitrogen supply to plants. It has been found that soybeans grown without cobalt are severely retarded in growth and prone to dying. Cobalt is added to some fertilizers for application to cobalt-deficient soil.

Cobalt (and hence B-12) deficiency causes loss of appetite, anemia, weight loss and finally death to ruminant animals like cattle, deer, camels and sheep. To prevent this, cobalt is either added to the grazing pasture or to the diet directly.

In humans, B-12 is synthesized by bacteria in the small intestine, and the cobalt is supplied from the vegetables grown on cobalt-enriched soil and from the milk of animals fed on cobalt-enriched diet. Vitamin B-12 may also be taken by humans as an ingredient of medicines to supplement the diet.

SUBSTITUTION

Cobalt is a scarce and costly metal. Hence efforts have been and are being made to conserve it to the maximum extent possible by trying other materials in some of the applications. In high-speed steel alloys, it has been found almost impossible to replace it without substantially compromising the performance efficiency.

For permanent magnet, various alternatives have been tried in the past. Amongst them, iron powder magnets developed in France before the 1950s, *bismanol* (comprising bismuth, manganese and iron powder) developed by US Naval Laboratory also before the 1950s, *ferroxdure* (an oxidic ceramic having the approximate composition $BaFe_{12}O_{19}$) developed in the early 1950s, and barium/strontium ferrites are worth mentioning. But they did not prove to compare favourably with cobalt-based permanent magnets in performance efficiency. Now, the neodymium-iron-boron (Nd-Fe-B) magnets invented in 1982, has emerged as a substitute of SmCo magnet in certain applications. But they suffer from some distinct disadvantages. For example, there is a marked decrease in their Curie temperature at above 120°C temperature, and they are susceptible to corrosion. Improvement has, however been reported in their corrosion resistance through coating and plating, but with increases in costs. Potential applications of Nd-Fe-B magnets are limited to those where the operating temperatures do not exceed 80°C (e.g., magnetic separators, magnetically levitated trains, brush-less wind power generators, MRI scanners).

In paint drier, there is an increasing demand for a substitute of cobalt soaps due to their carcinogenic nature. Dry alkalyd-based resins are emerging as possible substitutes.

But, the most viable scope for conservation of cobalt through substitution lies in increased use of the scrap.

COPPER

The name Copper is derived from Cuprum which in its turn originated from Cyprus, which was famous for this metal in ancient times (although it no longer produces copper, but its flag bears the copper-red colour to commemorate its ancient link with copper). The Romans who got much of their copper from Cyprus, called it “Cyprium aes” i.e., metal of Cyprus. Cyprium became corrupted to cuprum.

Copper along with lead and zinc is commonly referred to as *base metal* (‘base’ in the sense of ‘ignoble’, in contrast to the ‘noble’ metals gold, silver, platinum). It occurs in nature in the form of native copper or minerals. The principal economic minerals are chalcopyrites [CuFeS₂], chalcocite [Cu₂S], bornite [Cu₃FeS₃], enargite [3Cu₂S.As₂S₃], cuprite [Cu₂O], malachite [2CuO.CO₂.H₂O], and azurite [3CuO.2CO₂.H₂O]. thus broadly, the minerals can be grouped into two types –sulphide ores and oxide ores. Copper may occur as bedded deposits, veins, lodes. More rarely it may occur as dissemination in some types of granite, and since those granites have been found to be usually of porphyritic texture, such copper deposits are called “*porphyry copper*”.

HISTORY

During the stone age, man used to hunt with the help of crudely shaped stone “weapons”. It is believed that the earliest metal known to man was copper. The first record of use of copper and bronze dates back to about 6000 years ago (4000 BC) in Caucasian region, and to 5500 years ago (3500 BC) in Egypt and in Indus Valley. Copper was used in the water plumbing systems in the great pyramids. In 1991, in the Alps near Austrian-Italian border, some hikers found a fossil man with copper axe. Bronze articles dating back to 2200 BC were discovered in the same area. By about 500 BC, use of this metal spread to Phoenix, Persia and China. Copper is known to have been recovered from naturally leached deposits in China 2000 years ago. In the Lake Superior region of USA, archaeological excavations have unearthed arrow heads and spear heads made of copper, belonging to the period 1000-1500 BC. Mining of copper was known in Spain and Portugal during early part of Christian era, and these countries continued to be important copper-mining centres till the Medieval Period. Mining of copper in an organized manner commenced in Chile in 1601. In the USA, the first mining was recorded in the beginning of eighteenth century. But copper got the real impetus only during the second half of the nineteenth century with the development and popularization of electrical energy. The average annual world production of copper metal at the beginning of 19th century was of

the order of only 1825 tonnes. In 1880, this figure went up to around 175000 tonnes, and after a century, in 1992, it reached 8.9 million tonnes. In 2000, the world production of the metal was 13.2 million tonnes.

In India, the first record of copper occurrence was made by W. Jones in 1829 and that was in Singbhum, Jharkhand state. But the existence was definitely established by J.C. Haughton in 1854, when he came across some old workings. This led to the first mining of copper in 1857 by Singbhum Copper Company which, however, had to wind up in 1859 due to bad financial management. Thereafter, it was a history of starting and closing of mines and mining companies till 1924, when Indian Copper Corporation came into being and began systematic mining in Mosabani area. Between 1859 and 1924, various mining companies namely, Hindustan Copper Company, Rajadoha Mining Company, Cape Mining Company, Cordoba Copper Company, Ooregam Gold Mining Company etc. worked in the Singbhum area. In the post-independence (1947) era, exploration was started in an organized manner in Rajasthan and other areas in 1957, and mining projects were established. In 1967, the Indian Copper Corporation was taken over by the Government, and reconstituted into a new public sector undertaking – Hindustan Copper Limited (HCL). The HCL has since extended its mining operations to Rajasthan and Madhya Pradesh.

Parallel to the activities in Singbhum area, Bengal Baragunda Copper Company worked briefly during 1884 in Hazaribag area of Jharkhand, and Burn & Company worked in Bhotang area of Sikkim till 1914. Copper mining in Bhotang area has been restarted much later by a new company, Sikkim Mining Corporation.

The production of copper ore in India since 1910 has been as follows:

<i>Year</i>	<i>Production of copper ore</i>
1910	1000 tonnes (approximately)
1920	30000 tonnes (approximately)
1930	120000 tonnes (approximately)
1940	400000 tonnes (approximately)
1950	366000 tonnes
1960	448000 tonnes
1970	518000 tonnes
1980	2.1 million tonnes
1990	5.29 million tonnes
April,2000-March,2001	3.5 million tonnes

The production of copper metal (comprising cathode copper and electrolytic wire bars) during April,2000-March,2001 was only 264003 tonnes.

RECOVERY

The technology for recovering copper metal from its ore depends on the type of ore viz., sulphide or oxide, and on the grade or tenor of the ore. Earlier, lumps of high grade sulphide ores (copper metal

content of the order of 4% or more) used to be fed directly into blast furnaces. But now-a-days, such high grade ores have become scarce, and competitive economics does not permit the luxury of selective mining of high grade ore even if it occurs in a deposit. There are now two processes of recovering metal from the low grade ores produced from the present day mines namely, (1) the conventional technology comprising concentration, smelting, fire-refining and electrolytic refining; and (2) leaching. These processes are elaborated as follows:

1. Conventional technology: To this technology only the sulphide type of ores are amenable. Such ores (copper content in the range of 1-4%) are primarily treated by crushing, grinding and froth flotation to produce a concentrate, depending the tenor of the raw ore, the concentrate may contain up to about 30-40% copper (but usually less than 25% in India). This concentrate, when in a molten state, is called "*copper matte*", which contains, besides copper sulphide (CuS), iron sulphide (FeS) and other impurities. The matte is then smelted in a converter by blowing air. As a result, CuS gets oxidized to copper metal in molten state, FeS to FeO also in molten state, and sulphur is converted to SO₂ gas. Molten FeO being lighter than molten copper floats and is poured out as slag. The impure product obtained by smelting is called "*blister copper*" (it is so named because the surface is covered with blisters and vesicles created by the escaping gases). The blister copper is then either (i) fire-refined and cast into commercial billets, ingots etc. or (ii) directly cast into anodes for subsequent electro-refining.

- (i) *Fire-refining:* Fire-refining is carried out if the ore is free from precious metals like gold, silver etc. In this process, blister copper along with siliceous flux and coke is melted and agitated with compressed air. Sulphides of Fe, Zn, Sn etc. combine with silica to form a light silicate slag which is poured out completely. Pb, As and Sb form dross and are skimmed off, while the sulphur is eliminated as SO₂. In this process, however, part of the copper metal is also oxidized to form CuO. For reducing it a green wood pole is inserted into the molten bath. Burning of the wood yields CO gas which reduces the CuO to metallic copper.
- (ii) *Electro-refining:* If the ore contains gold and silver, then electro-refining is necessary. In the electro-refining process, thin sheets of pure copper cathodes and impure blister copper anodes are suspended in a bath of dilute H₂SO₄ acid and CuSO₄. When electric current is passed through the bath, the anodes dissolve and pure copper is deposited on the cathode sheets, while the associated metals like gold, silver etc. sink to the bottom of the tank and are recovered separately. The pure copper thus recovered is cast into wire bars, ingots, billets etc. and are sold.

2. Leaching: Leaching may be by two processes namely, (i) acid leaching or chemical leaching, and (ii) bio-leaching or bacterial leaching. The principles involved in the two methods of leaching are as follows:

- (i) *Acid leaching:* The oxide ore of copper is amenable to this process of treatment. H₂SO₄ acid is sprinkled on heap of CuO with the result that CuSO₄ solution is yielded readily due to weak affinity between copper and oxygen. Into this solution of CuSO₄, iron plates are immersed. FeSO₄ is produced along with impure copper metal in powdery form called "*cement copper*". This cement copper is then subjected to processing in the same way as blister copper by conventional technology.
- (ii) *Bio-leaching:* This process is suitable for treating very low grade sulphide ore (with copper content as low as say, 0.3% or even less). On a heap of ore, FeSO₄ solution is sprinkled. Bacteria originally present in the soil converts FeSO₄ into [Fe₂(SO₄)₃]. This reaction being

exothermic, heat is generated which in its turn increases bacterial activity. The bacteria, supported by air, oxidizes CuS to CuO and releases sulphur. The sulphur is then oxidized to SO₃ and finally H₂SO₄ is produced. The CuO and H₂SO₄ then react with each other to yield CuSO₄ and thereafter the process is same as in the case of acid leaching.

Depending on the location of the ore to be leached, the process is called (a) in situ leaching, (b) stope leaching, or (c) dump or heap leaching.

In India, acid leaching is practised in Malanjkhand copper mine to treat oxidized ore containing 1.2% Cu. Crushed ore is heaped in layers of 3 m height in leaching pits. The CuSO₄ solution that is yielded, contains 2-3 gm/litre Cu, and the cement copper contains (+) 85% Cu. Complete leaching of a 3 m high layer (about 33000 tonnes of ore) may take about 3 months time.

In Malanjkhand mine, experiments on bio-leaching are on a pilot plant scale. 3 m high layers comprising about 2000 tonnes of lean sulphide is treated at a time. The FeSO₄ solution yielded from acid leaching is used for the initial sprinkling of the layers. However, the yield is reported to be very slow, being only about 10% of the metal content in the first year with possibility of gradual decrease during subsequent years.

CRITERIA OF USE

- 1. Weak affinity for oxygen:** Due to weak affinity between copper and oxygen, copper does not undergo corrosion readily when exposed to air, and hence is rust-proof. It is this weak affinity which is taken advantage of in fire refining and acid leaching processes of recovering metal. Impurities tend to oxidize more easily than copper, and hence are separated out easily during fire refining. In acid leaching also, CuO readily reacts with H₂SO₄ to yield CuSO₄ solution.
- 2. Electrical conductivity:** Amongst metals, copper is the second highest conductor of electricity after silver. For the same volume of metal, the electrical conductivity of copper is 94% of that of silver (cf. aluminium 57%, iron 16%). Annealed copper is the international reference standard for comparing electrical conductivities of all materials – International Annealed Copper Standard (IACS) . The IACS value of copper is '100'.
- 3. Thermal conductivity:** Copper is an excellent conductor of heat. Its thermal conductivity is 0.941 cal/sec/cm²/°C.
- 4. Mechanical properties:** Copper is strong, yet extremely ductile and malleable.
- 5. Alloyability:** Copper can form alloys with a large number of metals.

USES

The important uses of copper metal are:

1. Electrical equipments and appliances
2. Electrical transmission and communication wires
3. Utensils
4. Alloys
5. Micronutrient
6. Pigment
7. Imitation Zari
8. Electronics

9. Refractory
10. Gem stone

These uses are elaborated as follows:

1. **Electrical equipments and appliances:** High electrical conductivity combined with the properties of high strength, malleability (hence workability) and corrosion resistance facilitates use of copper in pure metallic form (and also in alloy forms) in the manufacturing of generators, motors, switch boards, various household appliances like toasters, stoves etc.
2. **Electrical transmission and communication wires:** In this case high electrical conductivity combined with the properties of strength, ductility and resistance to corrosion is the key. High electrical conductivity enables even very thin wires to transmit electricity with minimal loss; and consequently, copper is particularly preferable in low tension transmission and telephone and telegraph wires, in which even a slight transmission loss makes a significant difference. Ductility and strength make it possible to draw metallic copper into very thin wires without breaking. The thinness of the wires has the additional advantage of rendering them very light; consequently, overhead transmission wires made of copper do not sag appreciably even if the poles are relatively far apart. The high resistance to corrosion is the key to the practically endless life of the overhead copper wires used outdoor.
3. **Utensils:** This is one of the oldest uses of copper. High thermal conductivity combined with strength, malleability and resistance to corrosion is the principal criterion. Strength and malleability facilitate working the metal into any desired shape, while thermal conductivity facilitates cooking in copper utensils. Due to the high resistance to corrosion, the household utensils made of copper possess very long life and are practically indestructible.
4. **Alloys:** Easy Alloyability, strength, malleability and non-corrosive properties render copper as dominant alloying component. The common but important alloys are described as follows:
 - (a) *Bronze:* This is one of the oldest alloys known. It contains mainly copper and tin, but other metals may also be added. It was a valued alloy in ancient times and even now bronze medals are the most valued after gold and silver medals for recognition of merit. In a special type of bronze called "*aluminium bronze*", tin is substituted by aluminium. The important bronzes are :

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Bell metal or speculum or beta-bronze or high-tin bronze	20–30% Sn; balance copper	High tin content makes the alloy brittle with poor ductility and hence not suited to engineering applications; used for casting into consumer articles like mirror, kitchen ware, idols, bells etc.
Phosphor bronze	87.75–89.5% Cu; 10–12% Sn; 0.25–0.5% P	Suitable for use in bearings of wheels including worn ones, which are under heavy load.

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<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Porous bronze	87% Cu; 10% Sn; 3% graphite	Used in small motors such as those of domestic appliances, starters of automobiles, business machines etc.
Leaded bronze	76% Cu; 9% Sn; 15% Pb; 2% Ni	Acid resistant bronze for use in poor lubricating conditions. Used in cranes and earth-moving equipment.
Wrought aluminium bronze	4–7% Al; may contain Ni, Fe, and Mn	Capable for deep drawing in cold operations, for resistance against corrosion and oxidation at high temperature; used imitation jewellery, cosmetic containers, pump rods, shafts, spindles etc.
High-duty aluminium bronze	Cu 79.5% ; Al 9.5%; Fe 4.5%; Ni 5.5%; Mn 1%	Superior corrosion resistance in marine conditions; also high wear resistance.
Gunmetal or Admiralty bronze	88% Cu; 10% Sn; 2% Zn	Corrosion resistant in marine conditions. Used in general utility construction parts.

The bronze technology was known since the ancient times – in many countries including India. The earliest known evidence of this technology in Indian subcontinent is the dancing girl of Mohenjo Daro which dates back to the 3rd millennium BC. Bronze casting in those times was by what is now called ‘*lost wax process*’. This technique has later been modified and has become known as ‘*investment casting*’. In lost wax process, first a wax model of the intended object is made. This model is then invested or coated with layers of clay (that is why now it is called investment process). The wax is drained out leaving a clay mould in which bronze is cast.

- (b) *Brass*: This is primarily an alloy of copper and zinc. According to an international study it has been found in 2006 that traditional brass containers help water remain bacteria-free more efficiently than stainless steel or plastic containers. The important types of brass are:

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
High tensile brass	Cu 55%; Zn 38%; Al 2%; Fe 2%; Mn 3%	Used where high-strength castings re required, as in marine propellers.
Die-casting brass	Cu 60%; Zn 39.5%; Al 0.5%	Used for general purpose die-casting works.
Brass	69–75% Cu; 21% Zn; 3–9 % Pb; 1% Sn	Suitable for valves, pressure tight castings, plumbers’ fittings, ornamental castings.
Naval brass	62% Cu; 36.75% Zn; 1.25% Sn	Good resistance to corrosion in salt water. Used in the form of sheets and extrusions.

In brass, lead is added to improve machinability. But US and Canadian restrictions on lead content in potable water setting the limit at 15 ppb at the tap, has forced manufacturers to go for lead-free brass for use in potable water pipe line fittings. A new kind of brass called 'SeBiLOY' was developed by replacing lead with selenium and bismuth. This alloy is now known as 'EnviroBrass'. Depending on usage, its composition varies as: 4-38% Zn; 6%(Max) Sn; 0.5-2.2% Bi; 0.01-1.1% Se; 0.5% (Max) Fe; 0.25% (Max) Pb; 1.0% (Max) Ni; 0.25% (Max) Sb; 0.05% (Max) P; 0.6% (Max) Al; balance Cu. Selenium and bismuth contribute to machinability.

- (c) *Ashta Dhatu*: "Dhatu" means either a metal or an alloy of metals. Ashta Dhatu literally means "eight metals" which are alloyed together. The metals (includes alloys also) are Au, Ag, Cu, Pb, Sn, Fe, bronze and brass. This was first made during the prehistoric era, presumably after the onset of the "iron age" i.e., later than 1800 BC, by mixing all the metals and their alloys that were known and available then. This marked the highest technological excellence of the day, and the alloy was reserved for making idols of Hindu deities only – an exclusive jurisdiction of the priests regarded with the highest dignity and honour in those days. Consequently, this alloy was considered very auspicious in Hindu scriptures, and is used now also, for casting icons for worship.
- (d) *Pancha Dhatu*: This means alloy of five metals (metal includes alloys also). The five metals and alloys are Sn, Cu, Pb, Fe and brass i.e., Ashta Dhatu sans the three most valuable metals/alloys namely gold, silver and bronze. This was first made during the prehistoric era probably as a cheaper substitute of Ashta Dhatu. Like Ashta Dhatu, this is also considered very auspicious in Hindu scriptures, and is used for casting icons for worship.
- (e) *Monel metal*: This was first made in 1905. It contains 66.0% Ni, 31.5% Cu, 1.35% Fe, 0.9% Mn and 0.12% C. Due to the predominance of nickel, its colour is almost silvery white and very attractive, and it is highly corrosion-resistant and hence durable, malleable and hence easily workable, and poorly magnetic. These properties make it useful in roofing sheets, shop fronts, food-cans, aircraft body parts, turbine blades, sinks, machine parts, chemical equipments, small fittings in marine craft etc.
- (f) *Cupro-nickels*: There are three varieties:
- 70/30 type cupro-nickel containing 68% Cu, 30% Ni, and 1% each Fe and Mn; it is highly corrosion-resistant in addition, it has high tensile strength. It finds application in oil coolers, tubes for salt water condensers for use in naval vessels, fuse wires etc.
 - 90/10 type cupro-nickel containing 88% Cu, 10% Ni, 1.5% Fe and 0.5% Mn; it is corrosion-resistant. It finds application in oil coolers, tubes for salt water condensers, fuse wires etc.
 - Constantan containing 55% Cu and 45% Ni; it has practically zero temperature coefficient of resistance and it gives a thermal electromotive force (EMF) against copper. It finds application in thermocouples for use at temperatures up to 400°C, and also in precision rheostats.
- (g) *German silver*: This is not silver, and is an alloy containing mainly copper, nickel and zinc. It is called so because of its bright silvery appearance. There are three varieties:

- 10% nickel silver containing 62% Cu, 10% Ni and 28% Zn; it is used in the form of sheet and strip for production of cutlery, tableware and decorative articles.
 - 18% nickel silver containing 55% Cu, 18% Ni and 27% Zn; it is used for making springs and contacts in telecommunication equipment.
 - Machinable quality nickel silver containing 46.5% Cu, 9.5% Ni, 41.25% Zn and 2.75% Pb; it has good machinability and can be machined into non-standard shapes for making various decorative objects.
- (h) *Damascene work*: Damascene work is an art of metal ornamentation. It has been defined by Sir Gregory Birdwood as the “art of encrusting one metal on another not in pieces which are soldered or wedged, but in the form of wire which, by undercutting and hammering, is thoroughly incorporated in the metal which it is intended to ornament”. The best living example of this work is the ‘*bidricraft*’ or ‘*bidriware*’ of Bidar in Karnataka, India, after which it is named. This craft is the Indian adaptation of the ‘*koftgari*’ work of Iran brought to India in 13th century. In this craft, gold or silver wire is encrusted on a metal body cast in a mould by the lost wax process (for details see bronze). The metal used in bidriware is copper and zinc in 1:16 proportion.
- (i) *Thermo-mechanically treated corrosion resistant steel*: Sheets of such steel containing 25% Cu with small amounts of Cr, Si and P is used for covering subsea portions of boats, ships etc. and also in applications requiring a high degree of corrosion resistance. Copper reacts with saline water electrochemically to form a layer of $[\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2]$ deposited on the steel surface. This compound is insoluble in saline water and protects the under-surface. In applications requiring resistance to atmospheric corrosion, the copper in the steel plugs the pores in the rust preventing passage of oxygen to the non-corroded surface.
- (j) *Marinel*: This alloy contains 18% Ni, 1.8% Al, 5% Mn, 1% Fe 0.7% Nb, 0.4% Cr and balance copper. It is characterized by high mechanical strength, resistance to marine corrosion and virtual immunity to hydrogen embrittlement in offshore subsea applications. This combination makes it suitable for use in bolting on naval vessels and in offshore pipeline rings, valve stems etc.
- (k) *Other alloys*:

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
18/18 austenitic corrosion resistant stainless steel.	0.07% C; 18.0% Ni; 18% Cr; 3.5% Mo; 0.6% Ti; 2.0% Cu.	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (e.g. chemical equipment).
Aluminium-copper-magnesium (Al-Cu-Mg)	—	Medium strength semis.
Aluminium-silicon	11% of fine Si particles evenly distributed in a matrix of Al with addition of 1% Cu.	High wear resistance, improved castability and corrosion resistance, decreased coefficient of expansion, elevated strength and ductility; used in pistons of automotive engines and bearings.

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<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Leaded aluminium alloys	Up to 10% Pb; 3-5% Cu; 0.5% Ni; 0.3-0.8% Mg or More than 10% Pb; small percentages of Cu, Mn, Zn, Fe and Si	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.
Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu ; Al-Si alloys containing 2-24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base	Used in self-lubricating bearings and other antifriction applications.
Aluminium-mica alloy	Mica coated with Ni or Cu with addition of Mg	Good solid lubricant; can be used in bearings.
Aluminium-copper-lead alloy	93.5% Al; 5.5% Cu and 0.5% Pb	Suitable for extruded bar sections amenable to be cut freely.
Aluminium-copper-bismuth alloy	93.5% Al; 5.5% Cu and 0.5% Bi	Used for mass produced components.
Aluminium-magnesium-manganese	97.8% Al; 1.0% Mg and 1.2% Mn	Uses requiring high resistance to corrosion such as in roofing material.
Aluminium-copper-magnesium-manganese	93.4% Al; 4.5% Cu; 1.5% Mg and 0.6% Mn	High strength with adequate workability; used in aircraft parts, truck wheels, etc.
Aluminium-copper-silicon-magnesium	86.5% Al; 3.0% Cu; 9.5% Si; and 1.0% Mg	Casting alloys used in automotive pistons etc.
Aluminium-silicon	6.3-11.0% of fine Si particles evenly distributed in a matrix of Al with addition of 1.0-3.5% Cu.	High wear resistance, improved castability and corrosion resistance, decreased coefficient of expansion, elevated strength and ductility; used in pistons of automotive engines and bearings.
Tin-based white metal or Babbitt metal	88.25% (min) Sn; 3-4% Cu; 7-8% Sb; 0.5% Pb	Used in automobiles and engineering works.
Manganin	Cu 86%; Mn 12%; Ni 2%	It has high electrical resistance and its thermal electromotive force (EMF) against copper is practically nil. It is used in precision electrical instruments like potentiometers, resistance boxes etc.

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<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Ternary copper-nickel-tin spinodal alloy	Cu 85%; Ni 9%; Sn 6% or Cu 77%; Ni 15%; Sn 8%	“Spinode” is a Greek word meaning cusp. This alloy is made by controlled thermal treatment called spinodal decomposition resulting in uniform dispersions of tin-rich phases in the copper matrix, and is characterized by high mechanical strength, high wear resistance and high corrosion resistance in sea water and acid environments. Used in high-productivity mould tooling for the plastic industry; high-performance bearings for aerospace and heavy duty mobile industrial equipment; and highly corrosion resistant components for undersea oil and gas exploration.
High beryllium copper alloy	Cu 96.8–98.4%; Be 1.6–2.85%; Co 0.065–0.35%	5-6 times stronger than copper alone, also high fatigue resistance.
Low beryllium copper alloy	Cu 96.70–98.35%; Be 0.25–0.70%; Co 1.4–2.6%	High electrical conductivity (60% that of copper alone), strong.

5. **Micronutrient:** Copper is a necessary ingredient in human diet. It helps formation of blood hemoglobin, and is beneficial for healthy bones, blood vessels and nervous system. It enters the system of human body from soil through plants and vegetables.
6. **Pigment:** CuSO_4 is used as a blue pigment. Impure unrefined blister copper can be used for manufacturing this chemical.
7. **Imitation Zari:** This is also called “*metallic Zari*”. Zari is a specially made thread used for fine embroidery by skilled artisans of India (specially Surat). There is a mention of this art in Prehistoric times of *Rig Veda* as dresses of gods and goddesses. However, this art flourished due to patronization of the Mughal kings of India during the Medieval times. In real Zari, silver wires are wrapped with gold paper, drawn and then wound around silk threads. In imitation Zari, copper wires are coated with silver (or sometimes with gold) by either electroplating or chemical process, wound around ordinary yarn, and then thinned to make fine threads of Zari. Copper wire for this purpose is redrawn wire made by heating ordinary thick wire with coal and then redrawing it into fine wire.
8. **Electronics:** The requirement for this application is of a very high-conductivity copper. The copper should also be immune from gassing or embrittlement when heated in a reducing atmosphere – a property specified for flame welding and for preparation of glass to metal seals. To meet these requirements oxygen-free high-conductivity (OFHC) copper is used. Such copper has to be specially made by remelting and pouring cathode copper entirely in atmosphere of carbon monoxide and nitrogen, so that no oxygen can be

absorbed. Such copper is characterized by less than 10 ppm oxygen, up to 2% higher electrical conductivity than normal cathode copper and higher thermal conductivity than normal copper.

9. **Refractory:** In Romelt technology (see chapter on iron ore - hematite) of steel manufacturing, water-cooled copper plates are used as refractory lining in the reaction zone.
10. **Gem:** A variety of malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) known as '*kidney stone*' (*Dane Phirong*' in India) is a semiprecious stone. It is green coloured with refractive index 1.90.

WASTE UTILIZATION

Wastes are generated right from the stage of treatment of ore to that of ultimate consumption. There are three important types of waste, for utilization of which, technology is available. These are as follows:

1. **Sulphur dioxide gas:** The commonest mineral of copper namely, chalcopyrite theoretically contains 35% S, 34.5% Cu and 30.5% Fe [cf galena- 13% S, sphalerite – 33% S]. This means that an ore containing say, 1% Cu will also contain about 1% S. In India the concentrates obtained by flotation, contain sulphur varying from 25-30 per cent. This sulphur is emitted as SO_2 gas during smelting and is a source of pollution. In many countries – particularly the developed ones – the environmental regulations are so stringent and so costly to comply, that they tend to serve a deterrent to free growth of copper smelting industry.

Technology has, of late, emerged for trapping this SO_2 and converting it to sulphuric acid (H_2SO_4). In India, capacities for production of H_2SO_4 have been set up in the smelters of Hindustan Copper Limited.

However, this technology does not always seem to be economically viable, unless there is ready consuming market of H_2SO_4 near the smelter requiring minimal transportation. Moreover, storage cost in industrialized countries, where level of H_2SO_4 consumption is already very high, and there is no consuming market near copper smelters, possibility of surplus supply situation of H_2SO_4 is a source of concern, because the environmental regulations create problems for its disposal also. On the whole, the problem seems to be not of utilization of SO_2 , but of the product H_2SO_4 .

In some mines, where both smelting of high grade sulphide ore and acid leaching of oxide ore go hand in hand, at least a part of the H_2SO_4 acid may be used in the leaching process.

2. **Ferrous sulphate:** During acid leaching of oxide ore, production of cement copper is accompanied by generation of waste FeSO_4 solution. This FeSO_4 can be partly utilized for the initial sprinkling of lean sulphide ore heaps during bio-leaching.
3. **Scrap recycling:** Even as early as the Greco-Roman times, broken bronze statues used to be remelted and resold in the form of ingots. Thus, recycling of copper products is not a new concept. Copper scrap can be classified into three broad types as follows:

- (1) *Fabrication (or new) scrap*: This comprises the chips and cuttings generated during production of metal and manufacture of semis. These are free from impurities and can be remelted straightaway without any need of refining.
- (2) *Used product (or old) scrap*: This comprises finished or consumer products discarded after use. These contain calculable amounts of copper. This scrap needs refining.
- (3) *Intermediate product scrap*: This contains assorted material generated during processing of copper metal, such as slag, dross, filter dust etc. Composition of this type of scrap is highly variable and unpredictable. Recycling of this scrap is not easy.

Of the three types of scrap, the old and new scrap are generally amenable to recycling economically. These scraps are called 'dross' in trade circle.

Copper can be recycled endlessly and the recycled copper has the same properties as primary copper. Moreover, energy consumption for production of recycled copper is significantly less than that of primary copper. Depending on the nature of scrap, the saving may vary from 50-90 per cent. But still, the world average recycling rate is rather low. Recycling rate is the ratio of the annually utilized quantities of copper scrap and the annual production of primary copper. According to an estimate made in 1992, the recycling rate in USA was about 60%, in Western Europe 50%, in Japan 47%, and the world average hardly 40 per cent.

One of the reasons of this low recycling rate could be the durability of the industrial products of copper. The lives of some common consumer durable products of copper are:

<i>Product</i>	<i>Life</i>
Cars	Over 8 years
Cables	Over 40 years
Buildings	over 80 years

Of the copper products, recycling of cable scrap is somewhat difficult. Cable scrap contains plastic. Though plastic can be removed by burning, it is prohibited by environmental regulations in many developed countries. The alternative process consists in granulation of the composite scrap followed by mechanical sorting through air classification. However, far more complex is the recycling of electronic scrap in which copper is mixed with a number of other metals, plastic, organic flame retardants and ceramics. Recycling of copper alloy scrap consumes more energy compared to copper scrap.

4. **Copper ore tailings**: For beneficiation, the run-of-mine ore is crushed to (-)200 mesh size. After flotation, the tailings contain some iron and minute amounts of manganese, zinc and copper. All these are micronutrients in soil. A technology has been developed by the University of Agricultural Sciences, Dharwad, India to use these tailings in agricultural fields so that these micronutrients are released slowly. According to a report, 20-30% increase in productivity could be achieved for cabbage, cauliflower, groundnut, maize, sunflower and sugarcane. These tailings can also be added to organic manures to the extent of 10-15% to make the latter micronutrient-rich.

- 5. Mine drainage water:** Technology has been developed for recovering copper from these wastes. Some copper present in the underground mine pillars goes into solution in the mine drainage water. This water is directed to flow over iron scrap which reacts with copper present in solution in the water; the metal precipitates as *cement copper*. The mine water can also be directed over old workings.

SUBSTITUTION

Though copper is relatively costly, it is indispensable in certain uses because of its unique combination of properties. However, in some of its uses, substitution is taking place. The common substitutes are as follows:

1. Aluminium:

- (a) Transmission wire:* Aluminium is substituting copper in electrical transmission wires – particularly in high tension wires. Electrical conductivity of aluminium is lower than that of copper, and hence thicker wire is required when aluminium is used. But aluminium being a light metal, the increased diameter does not make the wire very heavy. However, the high tension transmission lines are generally at considerable heights above the ground and hence some degree of sagging is tolerable. Also, a higher degree of transmission loss compared to low tension wires can be tolerated in case of high tension electricity transmission.
- (b) Utensils:* Aluminium is highly resistant to corrosion and is a good thermal conductor besides being less expensive. Consequently it has substituted copper in household cooking utensils.

- 2. Stainless steel:** Its high degree of resistance to corrosion and its thermal conductivity coupled with durability have enabled it to become a popular substitute of copper in utensils.
- 3. Steel, plastic and fibre glass:** These are finding increasing use in construction of buildings, manufacture of automobile bodies etc. in preference to copper.
- 4. Optical fibre:** This is a comparatively recent development in communication. In optical fibres, light, instead of electromagnetic energy (as in copper wires) or radio waves or microwaves (as in case of wireless communication systems), is used for carrying information in the form of video, voice or data. Optical fibres use the principle of successive total internal reflection of laser beam within a hair-thin glass fibre comprising an inner denser core surrounded by a lighter cladding – both highly transparent. Light is carried along the core due to total internal reflection at the contact surface between the core and the cladding, even if the fibre is bent. Data are coded into electric pulses which are emitted in the form of laser pulses. At the receiving end, the signal is converted back into electrical signals and decoded to get the output. Since there is no chance of any loss of light from within an optical fibre, data loss is practically nil. Also, since the frequency of light waves is over 1000 times greater than that of radio waves, the information-carrying capacity of an optical fibre is many thousand times more than that of a copper cable of similar thickness. Besides, optical fibres are highly resistant to fire, corrosion and temperature fluctuations. The longest optical fibre cable system is about 19000 km long and is laid under the Indian and Atlantic oceans, linking India with Europe and America. It has been commissioned in June, 1994.

GALLIUM

Gallium is an expensive and rare metal. It occurs in traces in coal ash, bauxite and sphalerite. Though its existence was predicted by D.Mendeleef in 1871, it was identified as a new element in 1875 by the French Chemist Lecoq de Boisbaudran, who coined for it the name 'gallium' after the Latin name of France, *i.e.*, Gallia.

Gallium is usually recovered as a byproduct during extraction of aluminium and zinc. In Bayer's process of alumina extraction from bauxite, the ore is leached with caustic soda to form sodium aluminate which may also contain a little sodium gallate. The latter can be precipitated as gallia from the residual solution left after precipitation of Al_2O_3 . From gallia, the metal gallium is obtained by electrolysis.

In the sulphuric acid leach process of zinc metallurgy, gallium chloride is extracted, which on electrolysis yields gallium. It can also be recovered from zinc flue dust.

CRITERIA OF USE

The most remarkable property of gallium is its low melting point (30°C) and high boiling point (about 1987°C). This combination of low melting point and wide range of liquid phase is unparalleled (cf. mercury has lower melting point, but it boils at only 357°C). In fact, it may liquefy when held in hand.

Gallium is extremely corrosive particularly at high temperature. It is a poor electrical conductor. It is capable of alloying readily with most metals. It is hard and brittle. It has high light reflectivity. Gallium is amenable to electron emission at low temperature and consequently at less current .

It has a radioisotope Ga-72, which is capable of absorbing gamma rays, storing them, and then emitting them slowly.

Gallium can form chemical compounds with other elements and those chemical compounds exhibit special properties.

USES

- (1) **Thermometry:** The unique combination of low melting point and high boiling point make gallium indispensable in high temperature thermometers and temperatures in the range of $500 - 1200^\circ\text{C}$ have been measured with such thermometers (mercury is not suitable as this

range of temperature which is well above its boiling point of 357°C). One of the problems with gallium is its extremely corrosive nature. For this reason, such thermometers are made of fused quartz tubes.

- (2) **Alloys:** Gallium is useful for making strong and low melting alloys. Its alloy with 12% tin melts at 15°C, while the alloy containing 60% tin, 30% gallium and 10% indium melts at below 15°C. The alloys gallium-magnesium, and gallium-nickel-silicon are very strong. However, gallium is too expensive to allow such alloys to be used for structural purposes; these may be suitable only in specialized applications (e.g., aviation industry). The poor electrical conductivity of gallium precludes its use in alloys of copper, silver etc. for making electric wires and conductors.
- (3) **Electronics:** The property of electron emissivity at low temperature makes gallium or its alloys useful for making cathode filaments in electron tubes. Such filaments emit electrons at lower temperature than conventional ones, and consequently the electron tubes need less electric current. Such tubes are especially suitable in portable receivers.

Gallium-phosphoride is useful for making liquid electronic devices for the purpose of read-out displays, indicator lights, outdoor signs and signals, etc. In this case, low melting point and easy electron emissivity are the key properties. When a surface, coated with a fluorescent chemical, is hit by beams of the emitted electrons, it glows.

Gallium arsenide is a semiconductor and is used in transistors, IC chips etc, particularly suitable in high frequency telecommunications and high speed computers (super computers). This compound is a powerful semiconductor material (See also the chapter on 'Germanium'). Gallium arsenide chips have several advantages over silicon:

- (a) Gallium arsenide chips are more radiation-resistant than silicon chips, and hence is considered suitable for use in satellites.
- (b) It can move electrons six times faster than silicon does, and consequently processing speed of chips made of the former is enormous compared to those made of the latter.
- (c) It can absorb sunlight faster than silicon does, and is more suitable in solar photovoltaic cells.
- (d) It can combine both light and electronic data processing on a single chip.

However, the major impediments for wide use of gallium arsenide are its cost and the extreme difficulty in making a perfect crystal. It is said that very small vibration or even gravity has a negative effect on it. The best crystals of gallium arsenide have been made in outer space – of course at a huge cost.

(4) **Other Uses:**

- (i) *Fire alarms:* On account of low melting point (See also the chapter on 'Bismuth').
- (ii) *Radiotherapy:* The radio-isotope Ga-72 has been used in treatment of certain types of cancer.
- (iii) *Catalysis:* Gallium-halides are useful.
- (iv) *Medicine:* Organic salt of gallium is believed to possess some curative effect on syphilis.
- (v) *Optical mirrors:* On account of its high reflectivity gallium is used for plating to reduce light absorption.

SUBSTITUTION

Research and development work for synthesizing some special kind of polymers that can conduct electricity is underway. These polymers, termed as '*conducting polymers*', when developed may substitute gallium in its use as semiconductor.

Advantage of a conducting polymer lies in its small size and light weight. R & D work on this is underway in various institutions in India.

GERMANIUM

Germanium is a scarcely found metal, often occurring as a trace element in sphalerite and coal. Its incidence in the earth's crust varies from 1-4 ppm. Germanium was predicted by Mendeleef in 1871, and was first isolated in 1886 by German chemist Winkler. However, it has come into focus of scientists only during the World War-II and thereafter.

Germanium is recovered from zinc ore, which is first roasted whereby both zinc and germanium are converted to oxides. These oxides are converted to chlorides. Germanium tetrachloride is then separated, hydrolyzed back into pure oxide and reduced to metal by heating with hydrogen. In U.K., germanium is being recovered on commercial scale, from flue dust.

CRITERIA OF USE

Germanium is a grayish white and brittle metal with high refractive index. It can transmit infrared rays easily. It is an important semiconductor material.

Semiconductors contain only a small number of loosely bonded electrons at room temperature, and hence their conductivity is very poor (of the order of 100000 times less than that of conductor metals). However, a characteristic feature of semiconductors is that their low electrical conductivity can be substantially improved by addition of minute quantities of "impurities" *i.e.*, foreign atoms of a different valency (*e.g.*, phosphorus, boron), and the process is called '*doping*'. These doping atoms or dopes serve as points of disturbance within the crystal lattice. Some types of dope lose electrons, thus facilitating flow of positive charge towards them; while other types collect electrons and thus, negative charges flow towards them. In the intermediate transition zone between these two types of dopes within a semiconductor, there is practically no flow of current, *i.e.*, the resistance is very high. Now, if an external voltage is applied to the semiconductor with its positively charged end connected to the positive pole and its negatively charged end connected to the negative pole, then the positive and negative charges of the semiconductor are both repelled towards the transition zone (similar charges repel each other). As a result, there will be high concentration of positive and negative charges in this zone causing intensive interchange of electrons, and a strong current will start flowing. On the contrary, if the poles of the external voltage are reversed (*i.e.*, the positive pole connected to the negatively charged end and the negative pole connected to the positively charged end of the semiconductor), then opposite charges will attract each other. As a result, the positive and negative

charges of the semiconductor will move away from the centre towards the external poles, and there will be no flow of current through it. Thus, a semiconductor allows flow of current only in one direction, and with increased output. This property is called '*rectifying property*'. If a semiconductor contains one transition zone, it is called a '*diode*'; and if it contains two transition zones, it is called a '*triode*' or a '*transistor*'.

A characteristic feature of the semiconducting behaviour of germanium is that the resistance to electricity decreases with rise in temperature (cf., in typical conducting metals, it increases).

USES

- 1. Thermistor:** Thermistors are extremely sensitive devices for measuring temperature. The property of decrease in electrical resistance of germanium with rise in temperature, is made use of in making of thermistors.
- 2. Electronics:** In the electronic industry, germanium is used in the manufacture of rectifiers (diodes) and transistors. The germanium rectifiers find use in radars for the detection of very high frequency electric waves. Transistors are used for amplifying the electrical output as in hearing aids, televisions, computers, small radio receivers etc. germanium-based rectifiers and transistors have the advantage that they are very small sized (consequently light in weight), shock-resistant and durable; and they require low power to operate.
- 3. Lenses:** The high refractive index of germanium has been made use of in the manufacturing of wide angle lenses of cameras and microscope objectives. In this application, germanium (instead of silica) is used as a raw material for glass.
- 4. Alloys:** Addition of 12% germanium to gold reduces the latter's melting point from 1024°C to about 367°C, and at the same time, colour and look of the 18 karat gold is retained.
- 5. Optical fibre:** Optical fibres are used for transmitting electromagnetic energy in the form of optical energy or light waves that travel through a thinner-than-hair tube by virtue of its total internal reflection from the walls of the tube. Total reflection occurs when light passes through a medium with higher refractive index and strikes a medium with lower refractive index at a low angle. An optical fibre is made of an inner core glass tube surrounded by a cladding also made of glass which is encased in a protective outer PVC jacket. In order that total reflection can take place within the walls of the core tube, the refractive index of the glass of the wall of the tube must be higher than that of the cladding glass. One of the methods to achieve this is by adding germanium to the glass used for making the core. Germanium, having higher refractive index, serves to increase the refractive index of that glass.
- 6. Other uses:**
 - (i) Measurement of strength of magnetic field.
 - (ii) Infrared optics for military weapon-sighting system.
 - (iii) Medicines.
 - (iv) Chemical compounds (*e.g.*, magnesium germanate).
 - (v) Catalyst in hydrogenation of coal.

SUBSTITUTION

Research and development works for synthesizing some special kind of polymers that can conduct electricity, are underway. These polymers, termed as '*conducting polymers*', when developed, may substitute germanium in its use as semiconductor. Advantage of a conducting polymer will lie in its small size and light weight.

Gold is the leader in the group of three metals commonly referred to as '*noble metals*'. The other two are silver and platinum. 'Nobility' of these metals emanate from their beauty of colour and lustre lasting intact over thousands of years, and their indestructibility, scarcity and high value. The average incidence of gold in the earth's crust is no more than a few parts per billion. Gold commonly occurs as native gold in a matrix of quartz. It also occurs associated with sulphide of copper. Varying amounts of silver usually occurs in association with gold. It occurs both as primary and placer deposits.

HISTORY

Gold is believed to be in use as early as 6000 years ago, but known records date back to a much later period. Occurrences of gold mines in Kerala, India were recorded in manuscripts dating back to 77 AD. Gold used to be mined in many Latin American countries such as Mexico, Peru, Bolivia, Chile etc. However modern gold mining commenced in 1801, when payable gold was discovered in USA for the first time. From 1853 till early 20th century, USA remained the leading gold producer in the world. Winning of gold in South Africa picked up in 1905, and until 1931 it remained the second largest producer of gold in the world. By that year, Russia and Canada became leading producers. By 1990, USA again became the largest producer followed by Australia. The World Production in 2000 was 2550 tonnes, in which the share of 8 countries namely (in decreasing order) South Africa, USA, Australia, Canada, China, Indonesia, Russia and Peru was 71 per cent. But the world's biggest mine is believed to be in Peru (Yanacocha mine), but some believe that Grasberg mine of Indonesia is still the biggest.

Though India was traditionally known for its gold, mining remained for the most part of history unorganized and unscientific. India's historical reputation was actually for the skills of the jewellers in mixing alloys, moulding, setting stones, inlay work, relief, drawing gold into fine wires, plating and gilding. From 1793 onwards, prospecting operations were consciously organized in different ancient mining areas of South India. In 1831, Nicholson discovered some rich pockets in Wynad hills of Kerala. The area was vigorously prospected from 1875 onwards, and a number of mining operations started. But soon they ceased. Kolar area of Karnataka first received attention in 1802, but it took as long as 69 years for modern mining to start in that area. Between 1871 and 1882, mining gained momentum, but by 1884 most of the mines closed down. Only one operation started by

John Taylor & Sons in 1880, survived and stood the test of time. After India's independence in 1947, the Bharat Gold Mines Limited (BGML) was created in 1956 in the public sector and it continued mining in the Kolar Gold Fied. Apart from this, another public sector undertaking namely, Hutti Gold Mines Limited (HGML) has been mining in the Raichur and Gulbarga districts of Karnataka. The Kolar mine has been closed down on 1st march, 2001, and presently, organized mining of gold in India is concentrated in the states of Andhra Pradesh and Karnataka only, and some production comes also through byproduct recovery of gold from copper smelters. Small amounts of gold is recovered in the unorganized sector by villagers who carry out crude panning of local river sands traditionally known as gold-bearing. An idea of the trend of production of gold (total of primary and byproduct) in India can be had from the following table:

<i>Year</i>	<i>Production (tonnes)</i>
1905	27
1947	5.34
1950	6.13
1954	7.35
1960	5.00
1970	3.24
1980	2.45
1990	2.21
April,2000-March,2001	2.62
April,2002-March,2003	3.05

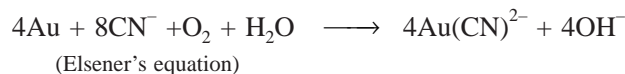
In recent times the share of primary gold in the total production has been varying from 83 to 89 per cent.

RECOVERY

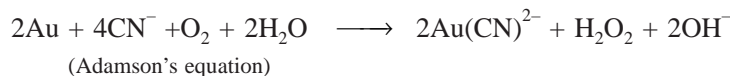
Gold is recovered in the form of bullions. Several simple and complex technologies are adopted for recovering gold depending on the type of ore/source. These technologies are as follows:

1. **Native gold in free state:** This is the simplest type of ore, and the process for its recovery is also simple – '*amalgamation*'. In this process, ground ore is allowed to pass over mercury-coated copper plates. Gold and mercury combine to form an amalgam which is scraped from the copper plates. After distilling off the mercury in retorts, pure gold is recovered.
2. **Native gold occurring in hard rock:** The technology for processing this type of ore is what is called '*cyanidation*' or '*cyanide-in-pulp*' or *cyanide leaching*. The ore is first crushed in cone crushers to 12 mm size. Then the steps are:
 - (i) The crushed ore is wet ground in tube mills to form a pulp containing 75% of (-) 75 micron size particles.

- (ii) The pulp is treated with sodium cyanide. The weak alkaline solution preferentially dissolves gold and silver particles. It is believed that the following reactions may take place:



And/or



The above complex reactions are believed to account for most of the free gold particles present in the pulp, and for this, adequate oxygen should be available.

- (iii) The solution containing gold and silver is passed through filters. The insoluble gangue is left behind as residue.
- (iv) Gold and silver is precipitated with the help of zinc dust added to the solution.
- (v) By smelting, zinc is driven off and crude bullions containing gold and silver are produced.
- (vi) Finally, silver is separated out by electrolysis and pure gold is obtained.

3. Very low grade ore and tailings from cyanidation process: There are two processes:

- (a) *carbon-in-pulp*: This is a recently developed technology. The principle depends on the ability of carbon to selectively adsorb gold semi-leached by calcium cyanide solution. For very efficient recovery, highly pure activated carbon particles (1 mm size) are used. When the gold concentration in carbon exceeds 0.2%, it is taken out and treated with hydrochloric acid to remove impurities. Then gold is stripped from carbon with the help of hot caustic cyanide solution, electro-won on steel wool cathodes, calcined, smelted and finally refined.
- (b) *Heap leaching*: Very low grade ore or tailings containing, say 0.4-0.7 gm gold is mixed with cement which acts as a binder. The mixture is then subjected to a slow rotary motion due to which pelletization takes place. The pellets are stacked in the form of beds on polythene sheets (to prevent leakage of cyanide solution into the ground), and irrigated with water containing 0.2% NaCN. After about 15 days of curing, an effluent somewhat richer in gold is obtained. From this effluent, gold is recovered by passing it through carbon in solution. By this process, up to 50% recovery of the gold contained in the original ore has been reported.

4. Complex sulphide type ore: The ground ore is first subjected to flotation process whereby float enriched in gold is obtained. From this float, gold is recovered by the carbon-in-pulp technology. If the ground ore consists of a mixture of native (free-milling) and sulphide types, then the two types are first separated by a gravity cyclone separation process. Separation takes place because sulphide type of ore is lighter compared to the native type. After separation, the fraction containing native gold is subjected to cyanidation and that consisting of sulphide ore is subjected to flotation and carbon-in-pulp processes described earlier. Such ore in Hutti mine, India has been subjected to bio-leaching with the help of *Thiobacillus ferrooxidans*. The recovery has been reported to be 95% in contrast to 30-40% by conventional process.

5. **Sea water:** In 2002, there was a research report claiming that it could be possible to extract gold from sea water by what is called '*immobilized liquid membrane technology*'. Sea water is known to contain about 10 ppm of gold. But still, it is not a proven commercial source of gold.
6. **Ultra-fine gold occurring in ore:** In some sulphide and arsenosulphide ores, the gold is often finely disseminated as submicroscopic particles. Prior to conventional cyanide leaching, these ores must be subjected to a pressure leaching or roasting pretreatment to free the gold particles for further treatment. But these processes are often not very efficient and considerable amounts of gold particles are not liberated. A process has been developed in 1990 in the US Bureau of Mines, by which the liberating efficiency can be improved by *bio-oxidation* with *Thiobacillus ferrooxidans* as the bacteria of choice. In the process, finely ground ore is inoculated with a culture of these bacteria which attack the ore matrix and free the gold particles.
7. **Scrap gold:** Recycled gold is an important component in the gold circulation. This is not waste after use (gold is indestructible), but re-processed for converting old ornaments to new ones. Such gold contains some silver and copper alloyed with it. There are two circuits of refining – gold circuit and silver circuit. In the gold circuit (Miller's process), the raw material is first melted and chlorinated; silver and copper are reduced to chlorides and skimmed off yielding gold of 99.95% purity. This is followed by the second stage (Wohlwill process) comprising electrolysis, yielding 99.99% pure gold. In the silver circuit, the chlorides of silver and copper are subjected to pyrometallurgical process in reverberatory furnace where copper is oxidized and separated from silver, and then the silver chloride is electrolyzed yielding 99.9 % pure metal.

CRITERIA OF USE

- (1) **Beauty:** Beauty is difficult to quantify or standardize. Gold has a typical golden yellow and it exhibits a bright glitter when polished. This combination of colour and lustre has been valued and treasured by mankind traditionally as 'beautiful'.
- (2) **Rarity of occurrence:** The rarity of gold deposits has resulted in consistent short supply of the metal vis-à-vis demand and has rendered it valuable throughout the past.
- (3) **Superstition and tradition :** Gold was originally sought and treasured by ancient man out of fear which gave way to superstition and finally to tradition. In the Stone Age, people sported ornaments made of teeth and bones out of belief that they will ward off evil spirits and cool down nature's anger. Around 5000 years ago, gold ornaments were used for much the same reason. That superstition became so much ingrained in the minds of people down the generations, that even now some occasions are designated as auspicious in some countries like India, when people – particularly women – must buy gold irrespective of whether they need or not. Rational thinking may not justify such purchases, but the forces of history and tradition are too strong to shun the habit.
- (4) **Indestructibility:** Gold cannot be destructively consumed. It is resistant to fire and ordinary chemicals. It can retain its physical, chemical and aesthetic attributes perpetually. This, coupled with scarcity, has been one of the main reasons for an almost all-pervasive tendency to grab and stock gold. This in its turn further widens the demand-supply gap.

- (5) **Malleability and ductility :** Gold is the most ductile and malleable of all metals. This property enhances its workability. It can be pounded to a thin leaf of 1/200000 inch thickness. One gramme of gold can be flattened to cover an area 50 cm × 50 cm.
- (6) **Electrical conductivity:** Gold has a high conductivity of electricity – 70 IACS or 70% of that of copper.
- (7) **Reflectivity:** Gold has high reflectivity at the red end of the spectrum of light.
- (8) **Alloyability:** Because of its softness, gold is generally alloyed with certain other metals like silver, copper, nickel, palladium etc.
- (9) **Specific gravity:** Metallic gold has high specific gravity of 19.33 due to which even a substantial quantity of gold occupies very little space.
- (10) **Streak:** Pure gold has a typical golden yellow streak which is seen when rubbed on the smooth surface of black fine grained jasper. This stone is used by goldsmiths in India for quick testing of the purity gold by comparing the colour of streak of any gold with that of pure gold. It is popularly called '*touch stone*'.

USES

It is believed that as much as 80% of the gold consumed in the world is used in ornaments, 15% for investment purposes and 5% for industrial applications. the purity of gold in trade circle, is expressed in terms of 'karat' (cf., carat used as a unit of weight for diamond etc.). Pure gold is 24 karats. The uses are as follows:

1. **Ornaments:** This is the oldest use of gold. In the beginning, fear and superstition were the main factors for sporting gold ornaments. Later on, scarcity, beauty of the colour and lustre have contributed to its role in serving as a status symbol. Its imperishability helps it to be preserved through generations and as long as one wishes. Its malleability and ductility enable it to be shaped into any design of the user's choice. Its capability to form alloy with copper is made use of in reducing its softness and in adjusting its hardness according to requirement. Iridium and ruthenium are also used for adulterating gold. In this application, 24 karat pure gold is not suitable. Generally 18-22 karat purity gold is used, but sometimes even 14 karat is also in vogue.
2. **Monetary reference and fiscal security of countries:** Imperishability and difficult availability are the principal criteria responsible for gold to be regarded as a reference base in settlement of all monetary transactions and disputes. This tradition is so ancient that through generations, it has become almost a part of human life and no alternative has been accepted. In the earlier times, gold coins were used directly for exchange of goods. Later on, when use of large number of coins became cumbersome, and paper currency replaced coins, gold bullion started to be used by banks as monetary reserve which served as the security backing for the currency notes circulated by them. This was called the '*gold standard*'. The gold reserve held by the bank of a country became a symbol of its fiscal strength. All major countries were on gold standard till World War-I (1914-18). During that war, many countries resorted to short sighted means by printing currency notes without any gold backing and went off the gold standard. By the time the World War-II (1940-44) ended, USA was the only country left with a currency backed by gold stocks. But in 1970, the US Government delinked dollar from gold. The following year, gold was officially

delinked from international currency, and later on in 1973, floating exchange rate was adopted. But still, there are many countries which regard gold backing of their currencies as a sign of fiscal strength – at least indirectly. In 1998, government-sponsored gold collection campaign in South Korea and sales from private sector in Indonesia to meet financial emergencies have demonstrated that gold continues to play its traditional role as a store of value and an asset of last resort.

- 3. Personal security:** In this use, imperishability, difficult availability (resulting in high value) and high specific gravity are the key criteria. Due to high specific gravity, a very small volume of gold can carry a very high value and thus, a highly valued piece of gold can be portable as well as easily concealable. In the earlier times, the value of gold as a personal security was universal. During those times, life and property were unsafe. In the face of bandits, drought, war, flood and greedy taxmen, no form of investment was safe; there was no bank to offer security of savings and no law to enforce contracts. Under such circumstances, gold had a significant advantage. Even a small piece carried high value, and it could be easily hidden from bandits and taxmen, and also during natural calamities or wars, people could flee with their gold (this was not possible with other forms of investments like land, house etc.).

The circumstances have changed drastically in recent times. Strong banking, insurance and legal systems have practically eliminated this use of gold, particularly in advanced countries. It is only in some societies with old traditional value systems in certain countries like India, China and the south Asian and Middle East regions, that gold is still valued as an insulation against inflation and insecurity.

There is another reason why many Indian women regard gold as personal security. Traditionally, the law did not provide them with the right to inherit ancestral wealth and properties. But the gold received by them in the form of ornaments or in other forms at the time of marriage (called '*Stree Dhan*') could not, according to law, be appropriated by their husbands' families. Now, the laws regarding inheritance have changed in favour of the women in India, but still, the traditional craze for gold has not died – partly due to social customs, partly due to ignorance and partly due to its easy liquidity.

- 4. Zari:** This is also called "*metallic Zari*". Zari is a specially made thread used for fine embroidery by skilled artisans of India (specially Surat). There is a mention of this art in Prehistoric times of *Rig Veda* as dresses of gods and goddesses. However, this art flourished due to patronization of the Mughal kings of India during the Medieval times. In real Zari, silver wires are wrapped with gold paper, drawn and then wound around silk threads. In imitation Zari, copper wires are coated with silver (or sometimes with gold) by either electroplating or chemical process, wound around ordinary yarn, and then thinned to make fine threads of Zari. Malleability of gold is the key criterion.
- 5. White gold:** Gold is too soft to be used in pure form for making jewellery, and it is usually mixed with certain other metals like silver, copper, zinc which do not modify the yellow colour of gold. In the 1920s, however, there was a craze in some western countries, for white alloys of gold, popularly called '*white gold*', which is fashionable even now. Nickel or palladium is added to gold for creating the white colour. White gold is sometimes rhodium-plated to give it a platinum look.

6. **Ashtadhatu:** ‘*Ashtadhatu*’ (or alloy of eight metals) is an alloy made up of Au, Ag, Cu, Pb, Sn, Fe, bronze and brass. This was first made during the prehistoric era, by mixing all the metals and their alloys that were known and available then. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship (see also chapter on copper).
7. **Medicine:** Gold has an important place in the traditional system medicines of India (Ayurveda). According to this system, pure gold is good for blood circulation, for mental health and for combating aging.

SPECIFICATIONS OF ORE

Specification of gold ore is expressed in terms of tenor *i.e.*, gold metal content. However, the actual tenor depends on the interrelationship of several factors as follows:

1. Type of ore: Gold ore may be

- (i) Nonrefractory
- (ii) Singly refractory
- (iii) Doubly refractory

‘*Refractory gold ore*’ means the ore which is difficult to treat. It has already been mentioned that cyanidation is facilitated in presence of oxygen. So the oxide type of ore (auriferous quartz) is most amenable to cyanide leaching and it represents the ‘*nonrefractory*’ type ore.

Presence of sulphide in ore poses problems inasmuch as it reacts with and consumes oxygen. Further, on oxidation, sulphide yields sulphuric acid which eats up the alkaline cyanide. Thus presence of sulphide inhibits gold recovery. It has also been mentioned that carbon particles adsorb gold, and this phenomenon is taken advantage of in the carbon-in-pulp technique by adding carbon to the cyanide solution **after** it is filtered out. If, however, carbonaceous matter (organic matter) is present in the ore itself, then adsorption starts as soon as cyanide is added *i.e.*, **before** filtration, and as a result the gold adsorbed by those carbon particles present in the ore, is left behind in the residue resulting in loss in metal recovery. If both sulphide and carbonaceous matter are present in the gold ore, then it is called ‘*doubly refractory*’. If one of them is present, it is called ‘*singly refractory*’.

2. Mode of occurrence of ore: Gold may occur in :

- (i) Primary deposits
- (ii) Placer deposits
- (iii) Tailing dumps

In primary deposits, gold usually occurs as disseminations in quartz reefs, in granite-diorite intrusions associated with pyrite, *etc.* The ore is required to be crushed and ground to liberate gold particles from the gangue. The crushing and grinding operations add to the cost of recovery. In placer deposits gold occurs as loose particles in sand and hence, crushing/grinding costs are much less. In tailing dumps, the unrecovered gold occurs in a matrix of gangue comprising silica, sulphides *etc.* in this case, the feed ore is already in very fine size, and crushing/grinding is not needed.

3. **Depth:** Depth is related directly to mining cost. Tailing dumps are overground source of ore. Placer deposits are near-surface occurrences. Primary gold deposits may be very shallow and amenable to opencast mining (*e.g.*, some deposits of Zimbabwe, less than

150 m depth); shallow and amenable to shallow underground mining (e.g., Hutti gold mine in India, around 600 m depth); or deep and amenable to very deep underground mining (e.g., erst while Kolar mine in India, up to 3200 m depth).

4. **Size of reserve:** Large low grade reserves of ore may yield the same quantities of metal as small deposits of high grade ore. In case of large deposits, bulk mining may have some cost advantages in terms of investments on processing and refining plants.
5. **Technology:** This has a vital role in determining the minimum tenor of the ore that can be worked economically. The conventional cyanide leaching technology is giving way to carbon-in-pulp technology. The tailing dumps, placer deposits and very shallow primary ore deposits are amenable to heap leaching followed by carbon-in-pulp technology. Primary ores containing upwards of 3.5 gm/tonne gold have been treated by conventional cyanide leaching technique; ores with lower contents of metal (2 gm/tonne) are treated economically by carbon-in-pulp technique; and ores containing gold as low as 0.4-0.6 gm/tonne have been reported to be amenable to heap leaching.
6. **Byproducts:** Gold is generally associated with silver. But various rare earth elements and other metals like platinum may also be present. If total recovery of the entire economic value contained in the gold ore can be achieved, then even low tenor of gold may prove to be economical.
7. **International price:** Gold being indestructible, is never consumed, yet is in demand. Whatever gold has been mined during the past 6000 years or so, must still be available overground in one form or another. Nobody knows for certain how much gold has so far been mined. Various estimates have been attempted at various points of time. According to one estimate made in 1970, a total quantity of 75000 tonnes of gold might have been mined till then; according to another made in 1980, the quantity could be 89000 tonnes. The Reserve Bank of India has, in 1994, estimated the world stock of gold at 128000 tonnes. The demand of gold, therefore, to a large extent, can be met through circulation of the already held gold, and not necessarily through fresh production from mines. As a result, the prevailing price may not be determined by the production cost. On the contrary, it is the international price that determines the limit within which the production cost has to be maintained. This in its turn determines the lower limit of the tenor at which gold ore can be mined economically at a given point of time.

The relationship between the tenor of gold ore on one hand and the different factors on the other hand can be summed up thus: the specified gold content in the ore can be lower and lower with

- (i) Decreasing content of sulphides and carbonaceous matter
- (ii) Decreasing compactness of the ore
- (iii) Decreasing depth of occurrence of the ore
- (iv) Increasing size of the deposits
- (v) Advancement of technology
- (vi) Increasing recovery of byproducts
- (vii) Increasing international price

The gold content of the lowest grade that has been mined and processed in modern times, has been reported to be 0.4 gm/tonne.

WASTE UTILIZATION

Tailings from Kolar gold mine, India which consisted of scheelite, were in the past tried for recovering tungsten concentrate. Recently, in 2002, it has been reported that the tailings which contained minute amounts of manganese, zinc, copper etc. can be used in agricultural fields to enrich the soil with these micronutrients.

Fine gold particles flying from the gold smithies get into the dusts. It is a common practice to collect these dusts and recover the gold particles by panning.

INDIUM

Indium metal was first discovered in 1863, and it owes its name to the “indigo” lines it produces on being subjected to spectroscopy. No natural ore of indium is known, but its incidence in the earth’s crust is estimated as 100 ppb. It is found in economically recoverable quantities in association with some sphalerite deposits. Its potentiality as a useful metal was first recognized in 1924, and during World War-II, demand for this metal started increasing significantly.

CRITERIA OF USE

Corrosion resistance and slipperiness are the two properties that stand out prominently in most of the industrial applications of indium. The different criteria of its use are as follows:

- (1) **Melting:** It has a low melting point of 156.4°C. Molten indium is highly viscous and the viscosity is consistent over a wide range of temperature.
- (2) **Hardness and strength:** It is by itself so soft that it can be scratched by nails, but at the same time it has a fairly high tensile strength of 380 psi and is able to impart hardness and strength to other metals alloyed with it.
- (3) **Alloying ability:** It is easily alloyable with a wide range of metals like gold, silver, lead, copper, cadmium, tin, zinc, bismuth etc.
- (4) **Corrosion resistance:** It is highly resistant to corrosion and tarnish. In this property, it is superior even to gold and silver which tarnishes after prolonged use and exposure, and to lead which dissolves in certain organic acids.
- (5) **Surface property:** It is highly slippery in feel. It has a high degree of ‘wettability’ and it is capable of adhering to both glass and metals, and also to other surfaces when rubbed across them.
- (8) **Colour and lustre:** It is bluish white and highly lustrous metal capable of reflecting all colours of light.
- (9) **Chemical reactivity:** It reacts with oxygen, sulphur, halogens etc. to form different chemical compounds some of which have useful properties like fluorescence, photoconductivity, pleasing colours etc. For example, the sesquioxide has yellow to orange colour, the oxide and sulphide possess fluorescence as well as photoconductivity, and the arsenide, antimonide and phosphide are good semiconductors.

USES

- (1) **Bearings:** Indium is added to alloys of silver with lead, copper, cadmium etc. that are used in bearings, particularly those required to withstand high load (e.g., aviation engine bearings). The key criteria in this application of indium are:
- (i) Slipperiness, due to which lubrication is facilitated;
 - (ii) Wettability, due to which the oil film applied to bearings adheres to it;
 - (iii) Resistance to corrosion by organic acids formed from the lubricating oils due to the heavy load;
 - (iv) Capability to harden lead, silver etc; and
 - (v) Consistency of viscosity of the molten indium formed under the heat generated in the bearings, which increases its lubricating efficiency.

The deficiencies of indium are compensated by other alloying metals. For example, silver imparts fatigue resistance (i.e., resistance to repeated stress) to the bearings, lead provides resistance to acids (other than organic acids) and likewise.

- (2) **Dentistry:** Indium was first used in an alloy for dentistry in 1934 and it was the first commercial use of indium. Low melting point, smooth lustrous finish and high resistance to tarnish are the key criteria. Besides, it imparts strength to gold, with which it is usually alloyed for this application.
- (3) **Plating:** Indium is used for plating the surfaces of silver, lead, cadmium, zinc, tin, gold, copper etc. Abilities to impart strength to the surface, to increase its tarnish resistance, and to impart highly lustrous finish to the surface, and above all, the high degree of wettability are the principal criteria in this use. Due to the latter factor, indium adheres to the base firmly, and does not peel off.
- (4) **Sealing:** Indium alloyed with lead, tin and bismuth is used for vacuum tight sealing in applications where high efficiency is specified, such as in gaskets of cryogenic appliances. The principal criterion is its wettability, i.e., ability to firmly adhere to glass and metals alike. This ensures no gap between the sealed edges and the sealing material.
- (5) **Dyes:** Indium is particularly preferred in the dyes meant for casting and drawing of wires. Indium (i) increases the life of the dyes by virtue of its strength and corrosion resistance and (ii) facilitates smooth and fast drawal of wires by imparting slipperiness to the inside surface of the dye.
- (6) **Solder and brazing material:** Basically, solder is an alloy of lead and tin and brazing is brass used for joining metals. Various other metals may also be added to adjust the properties to suit specific needs. Indium is added to adjust melting temperature, strength and corrosion resistance of the soldered/brazed joints. By adding indium, strength up to 5200 psi and melting temperature up to 520°C can be achieved. Indium alloys are required for soldering of delicate and precision parts in computers, electronic equipments etc.
- (7) **Motion picture screens and mirrors:** Lustre and ability to reflect all colours are the principal criteria in this application.
- (8) **Compounds:** Affinity of indium to oxygen, sulphur, arsenic, antimony and phosphorus facilitate formation of various indium compounds which, by virtue of their special properties, are useful in the following applications:

- (i) Glass: Indium sesquioxide is a light yellow to dark orange colouring agent.
 - (ii) Electric industry: The oxide and sulphide of indium are fluorescent.
 - (iii) Infra-red detection: The oxide and sulphide possess a high degree of photoconductivity, and are sensitive to even invisible infra-red rays.
 - (iv) Semiconductors: Arsenide, antimonide and phosphide of indium are strong semiconductors. Along with germanium, these are used for making high speed diodes such as the laser diodes used in optical fibre junctions.
- (9) **Alloys:** Indium is added to different metals and alloys with a view mainly to lowering the melting point. Indium-containing alloys are used for applications requiring low melting point. Examples of metals with which indium is alloyed, are bismuth, lead, tin, cadmium, mercury, gallium, etc.

LEAD

As has been mentioned in the chapter on copper, there are three metals commonly referred to as 'base metals', and lead is one of them, the other two being copper and zinc. Lead metal being the ultimate radioactive decay product, occurs in native state in small amounts associated with radioactive minerals. However, the most common economic mineral of lead is galena (PbS), which may sometimes alter to cerusite (PbCO_3) or anglesite (PbSO_4). Galena may occur in a uni-metal deposit (e.g., Agnigundla in Andhra Pradesh and Sargipalli in Orissa), or in a bi-metal deposit of both galena and sphalerite (ZnS) in economically recoverable quantities (e.g., Zawar and Rampura-Agucha in Rajasthan) or in a multi-metal deposit containing lead, zinc and copper ores (e.g., Rangpo in Sikkim, Ambamata in Gujarat). The common host rocks may be dolomite, calc-silicate, quartzite or schist. Silver is often present in solid solution with galena.

HISTORY

It is believed that the Chinese knew the use of lead metal as early as in 2000 BC. Definite evidences of the use of lead by the ancient Egyptians, Greeks and Romans in ornaments, weights, solder and water pipes have been unearthed. During the middle ages, important centres of lead mining developed in Spain, Sweden and Eastern Europe. In USA the first lead mine started in 1621.

In India, some sporadic mining in small scale was done in the past in Bihar to cater to local needs. During the period 1850-1905, attempts were made to mine various deposits scattered in Bihar by some companies, but all such operations met with either no or limited success. The old workings of Zawar in Rajasthan were opened up in 1945 by M/s Metal Corporation of India. It set up a concentration plant near the mine and a lead smelter in Tundoo in Bihar. In 1966, this company was taken over by a public sector corporation, M/s Hindustan Zinc Limited. Subsequently this company started recovering lead from various other deposits in Rajasthan, Orissa and Andhra Pradesh. This public sector company has recently been privatized but the name remains the same.

The world production of primary lead metal was less than 250000 tonnes during the early part of nineteenth century. It increased to about 415000 tonnes in 1880, to over one million tonnes in 1900, to over 2.1 million tonnes in 1925, and to about 3.5 million tonnes in 1968. subsequently, it has decreased to about 3.2 million tonnes in the 1990s.

The production history of primary lead metal in India is as follows:

<i>Year</i>	<i>Production</i>
1947	639 tonnes
1950	639 tonnes
1960	3745 tonnes
1970	1861 tonnes
1980	14846 tonnes
1990	24747 tonnes
April, 2000-March, 2001	34840 tonnes

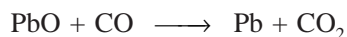
In the recent times, the ratio of secondary lead to primary lead in the production has been about 7 per cent.

RECOVERY

Lead ores are not directly amenable to metallurgical processing. The ores are first concentrated, then smelted and finally refined. A process was developed in 1990 by US Bureau of Mines in which the concentrate was leached instead of smelting.

- (a) **Concentration:** Concentration of simple uni-metal ores containing galena requires simple gravity concentration or simple flotation techniques. However, such ores are relatively uncommon. Bi-metal ores containing lead and zinc and multi-metal ores containing lead, zinc and copper need complex techniques of differential flotation. First, zinc and iron (pyrite) are depressed while lead and copper are floated. Next, lead and copper are separated into lead and copper concentrates. Then, zinc is floated to produce zinc concentrates. Finally, pyrite is floated while other gangue minerals are depressed and rejected as tailings. Ores associated with calc silicate rocks and dolomite are comparatively easy to beneficiate. However, multi-metal ores, in most cases, pose problems in producing clean concentrates of acceptable grades and recoveries, mainly due to interlocking texture resulting in high tailing losses. Further, ores associated with graphite, mica and talc are generally not easily amenable to beneficiation. These minerals being flaky in form, cannot be easily depressed in preference to lead. In India, lead content in the different concentrates produced from different ores (containing 0.72-2.20% Pb) varies from 40-75 per cent. Silver values, if present, are carried into the lead concentrate.
- (b) **Smelting:** Smelting of the concentrate may be carried out either in an ore furnace (in case of simple uni-metal ore) or more commonly, in a blast furnace (in case of complex ores). The essential principle of smelting comprises oxidation and reduction.

In ore furnaces, the charge consisting of a mixture of lead concentrate and coal or coke, is oxidized by blowing air. Part of the PbS is oxidized to form Pb, PbO and SO₂, while coal is oxidized to CO₂ and CO. the PbO is then reduced by the unoxidized PbS and the CO gas according to the reactions:



For smelting in blast furnace, the lead concentrate is first roasted at 1400°C to form PbO sinter and SO₂. Then the PbO sinter (containing impurities like zinc and other metals) is mixed with coke and flux (lime or silica) to form the charge for the blast furnace. Air is blown through the charge raising the temperature to 1400°C and oxidizing coke to CO gas, which in its turn reduces PbO to metallic lead. The molten lead (it still contains some precious and other metallic impurities) settles down at the bottom in the form of bullion, while zinc and certain other metals combine with the flux to form an upper layer of slag which is poured out.

- (c) **Leaching:** Galena concentrates are leached directly under oxidative conditions in fluorosilicic acid at temperatures less than 120°C. This dissolves the lead and produces a residue containing elemental sulphur and other metal values. This process can do away with the high temperature smelting altogether, and thus save energy and also the SO₂ emissions are avoided. Thus, this process may be environment-friendly and energy-saving.
- (d) **Refining:** Refining essentially consists of three broad processes namely, (i) dressing, (ii) pyrometallurgical refining and (iii) electrolytic refining. The first two processes are employed for the lead bullion obtained from smelting, while the third one for lead obtained from both smelting and leaching.

In dressing, impurities are made to rise and form a scum on the surface of the molten metal, and then that scum is removed. First, the bullion of lead is softened just above its melting point, and then agitated after adding elemental sulphur to it. Sulphur reacts with copper to form CuS due to its stronger affinity to copper than to lead. The scum of CuS is dressed out. This process is also called 'softening'.

In pyrometallurgical refining process, the softened bullion is heated to a higher temperature to form a molten bath. Upon vigorous agitation, surface oxidation takes place, and insoluble oxides of tin, arsenic, antimony etc. are removed. Then silver and gold are removed by adding zinc dust which form gold-silver-zinc crust on the surface of the bath. By this process, 99.95–99.99% pure pig lead is produced.

Certain impurities like bismuth can only be removed effectively by electrolytic refining process.

CRITERIA OF USE

The unique combination of acid-resistance, softness and heaviness is the key to most of the practical uses of lead. The important criteria are as follows:

1. **Softness:** Lead is the softest and the most malleable of all the base metals, and consequently, it can be easily worked and fabricated.
2. **Specific gravity:** It is the heaviest of base metals. Its specific gravity is 11.34 at 16°C (cf., specific gravity of copper is 8.96 and that of zinc 7.13).
3. **Melting point:** It has relatively low melting point of about 327°C (cf., melting point of copper is 1083°C and that of zinc 420°C). consequently, it is easily castable.
4. **Ductility:** Its ductility is poor, but that is made up by softness and low melting point.

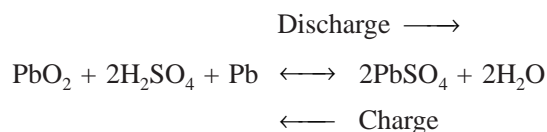
5. **Acid resistance:** Amongst the common metals, lead is the most resistant to corrosion by acids. It dissolves very slowly in nitric acid and is highly resistant to sulphuric and hydrochloric acids.
6. **Alloying ability:** Lead can be alloyed with metals like tin, copper, calcium, arsenic, silver, strontium, bismuth and cadmium which impart strength to this soft metal.
7. **Chemical affinity:** Lead forms a number of chemical compounds, but its affinity for oxygen is particularly strong. The ease with which lead oxides are formed, is taken advantage of in smelting of lead. Besides, this affinity is partly responsible for resistance of lead to acids and to atmospheric oxidation. Lead quickly creates a protective oxide cover, which then prevents further oxidation. However, its affinity for the radical SO_4^{--} is relatively weak (compared to other base metals), and consequently, the chemical reaction yielding PbSO_4 can be easily reversed by strong electric current.

USES

1. **Storage battery:** This is also called '*accumulator*' or '*lead acid battery*', and it consists of two or more secondary cells grouped in a battery. The principle underlying the working of a cell is that if two different metals are immersed in an electrolyte, then their differential solubility generates a difference in voltage, and one of the metals appears to be positively charged (anode) in relation to the other which appears to be negatively charged (cathode). In this process, the chemical energy of the metals and electrolyte is converted into electrical energy. If in this process, the metals and the electrolyte are consumed irreversibly, then the cell is called '*primary cell*'. On the other hand, if the chemical energy can be restored through reversion of the chemical reaction by electric current, the cell is called '*secondary cell*'.

In a common type of secondary cell, first designed in the 1880s and called '*flooded lead-acid battery*', plates of lead are immersed in an aqueous solution of H_2SO_4 acid, which is a conductor of electricity. In this application, lead is used mainly because of its resistance and weak affinity to H_2SO_4 acid (particularly the radical SO_4^{--}), as a result of which the chemical reaction between lead and H_2SO_4 can be easily reversed.

In the neutral state, to begin with, both the anode and cathode plates are coated with litharge paste (PbO). During charging of the cell, when electric current is passed through the plates and the electrolyte, the oxygen of the negative plate goes and joins the PbO in the positive plate. As a result, now the charged cell will consist of an anode of PbO_2 and a cathode of porous lead sponge. During discharging, a series of complex chemical reactions takes place amongst the plates and the electrolyte, as a result of which PbSO_4 is formed on both the plates, and the H_2SO_4 acid is consumed. But in the process, the chemical energy of the aqueous H_2SO_4 acid is converted into electrical current. Again, when the cell is charged, the PbSO_4 breaks up into PbO_2 and Pb releasing the radical SO_4^{--} into the electrolyte solution, thus restoring the chemical energy. The actual reactions that take place within the cell are complex. But the broad principle can be illustrated by the following simplistic model:



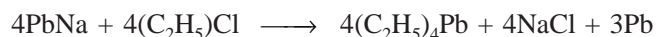
In the flooded lead acid battery, water has to be added at regular intervals as it is lost during operation. Such batteries find use for providing the starting power in trucks, cars, submarines etc. and also for stand-by power in houses. But in a modified version called '*valve-regulated lead acid battery*', developed during the 1960s, the battery is sealed and the gases that are produced during operation are recombined, minimizing water loss. It has become the accepted power source for computer back-up, telecommunications and emergency power systems, and for cordless tools and appliances, electric vehicles etc.

In practice, various other modified and improved versions of this cell are used depending on performance requirements. The different types are:

- (i) *Lead-antimony battery*: Instead of pure lead metal, its alloy with antimony is used. While antimony stiffens the plates, it also causes self-discharge more rapidly by creating hard lead sulphate crystals.
- (ii) *lead-calcium battery*: Batteries made of lead-calcium plates have low self-discharge as long as the weather is not too warm. Once fully charged, they do not require recharging for several months.
- (iii) *Lead-calcium-tin absorbed electrolyte battery*: In such a battery, plates are made of lead-calcium-tin alloys, and the electrolyte is captured in a fiberglass matter forming a gel. the rate of self discharge is extremely low.

- 2. Anti-knocking additive:** An internal combustion engine is designed in such a way that a perfectly timed spark should ignite a flame that will propagate smoothly through the charge. But the complex chemical structure of gasoline does not usually allow a perfectly timed spark. Rapid build-up of HO₂ radicals may take place and a portion of the fuel charge explodes prior to the arrival of the flame point. This produces an audible sound associated with vibration in the engine, which is called '*spark knock*'. An anti-knocking substance added to the gasoline serves to reduce this spark knock and to increase the efficiency and life of the engine. This phenomenon is related to what is known as '*octane number*' of the fuel i.e., the ratio of the content of octane to that of heptane in the gasoline (see also the chapter on sodium).

Not lead as such, but a compound called '*tetraethyl lead*' [(C₂H₅)₄Pb] is a good anti-knocking agent. Tetraethyl lead is manufactured by treating an alloy of lead and sodium (Pb₉₀-Na₁₀) with ethyl chloride (C₂H₅Cl) according to the reaction:



Only 2–3 ml of tetraethyl lead is added per gallon of gasoline.

In this use, the property of lead that counts is its ability to form alloys and chemical compounds. The mechanism of the anti-knocking performance involves decomposition of tetraethyl lead into a nonstoichiometric lead oxide (a nonstoichiometric compound is the one in which a fraction of given atom is either missing or in excess); this lead oxide is capable of trapping the HO₂ radicals, which are mainly responsible for the spark knocks.

- 3. Cable sheathing:** For low to medium frequency electrical power transmission, single conductor wires may be sufficient. But for transmission of certain high frequency electromagnetic signals (radio, radar, television), such wires are not suitable because of :

- (i) high electromagnetic radiation losses, and
- (ii) inductive interference or 'cross-talk' resulting from electric and magnetic field coupling between adjacent lines.

For this purpose, simple co-axial cables are used. In such a cable, there is an inner conductor surrounded by a tubular outer conductor, separated by an electrically insulating air space which confines the electric and magnetic fields. This whole cable may be sheathed by a jacket of polyethylene to reduce the interference of external fields to the minimum.

However, in a long distance communication system requiring a very high telephone channel capacity (carrying capacity of the order of, say, 132000 telephone calls), the following conditions must be fulfilled:

- (i) Total insulation against loss of electromagnetic radiation and interference from external source.
- (ii) Total insulation against 'cross-talk' due to field coupling.
- (iii) Dimensional precision throughout hundreds and thousands of kilometers of cable length.

To serve this purpose, multi-coaxial cables sheathed by a series of insulators comprising paper wraps, high density polyethylene jackets, thermoplastic cement and lead are used. The lead sheath provides:

- (i) A shield against loss of high frequency radiation losses by virtue of its high density and resultant absorbing capacity.
- (ii) By virtue of its softness, some reasonable mechanical strength to the cable without sacrificing flexibility to any great extent.
- (iii) Dimensional precision by virtue of its ability to be extruded in a continuous sheath around the internal conductors (this is facilitated by the low melting point, softness and workability of lead).
- (iv) Protection against moisture.

For making optimum adjustments of the various properties, lead used as a cable sheath, is generally alloyed with arsenic (0.15%), bismuth (0.1%), tin (0.1%) and antimony (1.0%).

- 4. Vibration damping:** In the construction of multistoried building, pads made of lead and asbestos are placed as barriers between the ceilings and the walls and also below the structure. These pads serve to absorb vibrations generated due to noise. The high density of lead (and consequent compactness and coherence of the atoms) makes lead suitable in this application.
- 5. Radiation shielding:** Here again, the high density of lead enables it to be used for shielding radiation in atomic reactors, X-ray machines, high-altitude flying aircrafts etc. Lead is also added for making special glass meant for use in window panes in the vicinity of X-ray machines and atomic plants.
- 6. Bullets and shots:** For manufacturing lead shots, lead is melted, and then the molten lead is dropped from a height (generally 40 m or so) into water; the lead droplets instantaneously freeze in the form of spherical shots. In this process, the low melting point

of lead is one of the main criteria. The other main criterion is the high density that imparts maximum striking power with minimum air resistance to the falling droplets as well as to the finished shots when fired.

7. **Acid tanks:** Due to its high resistance to sulphuric acid, lead is a suitable material in the tanks meant for handling sulphuric acid. For improving the chemical resistance, lead may be alloyed with 0.06% Cu or 1.12% Sb.
8. **Plumbing:** This is one of the oldest uses of lead. Water pipes made of lead are known to be in use during the Roman period. In fact, the word 'plumbing' is related to the Latin word 'plumbum' meaning lead. For making water pipes, the corrosion resistance of lead and its easy workability are the principal criteria. The poor strength does not come in the way, because water pipes are not required to withstand much load. In pipes meant for transporting chemicals, lead is preferred due to its acid resistance.
9. **Roofing sheet:** In this application, iron sheets plated with tin containing some lead is used. For this, what is called "*terne-plating*" of iron sheets is carried out. The term "*terne*" is a French word meaning dull. The addition of lead makes the tin dull. The technology of *terne-plating* is similar to that of tin-plating. The positions of tin and lead in the electromotive series are close to each other, and their ions move together towards the iron surface (cathode) to be plated. This closeness is made use of in *terne-plating*. Lead reinforces the weather resisting capability of tin.
10. **Solder:** Solder is an alloy of tin and lead, which is used for joining two pieces of a metal by a process of welding called "*soldering*". It is sometimes called "soft solder" to distinguish it from "silver soldering" which is hard and which contains neither tin nor lead. Early Romans used two types of solders – very soft *Tertiarium* containing lead and tin in 2:1 ratio, and somewhat harder *argentarium* containing lead and tin in 1:1 ratio. The latter type is commonly used now-a-days. In solder the role of lead is to soften it, and that of tin is to lower the fusion temperature as well as to strengthen the bond by virtue of its adhering power. However, soldering is not a suitable welding process for very high temperature applications requiring a very high strength of the bond. But, on the other hand, it is the most suitable process where (i) high temperature may melt and damage the parts to be joined, and (ii) precision – more than strength – is required. Electronic parts of television, computer etc. may be cited as examples.
11. **Pigments:** Lead pigments are corrosion resistant. The following compounds of lead are used:

White lead	$2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$
Red	Pb_3O_4
Blue lead	$\text{PbSO}_4 \cdot \text{PbO}$ combined with ZnO and C
Dyes in Yellow, Red, Orange and Green paints	Lead chromates

12. **Oil drier:** Oil, paints and varnishes dry by the uptake of oxygen. The exact mechanism by which the drying takes place, is not known. But it is believed that the unsaturated fatty acids in oils make them reactive and they attract great amounts of oxygen causing

polymerization. This ability of unsaturated oils make them form a solid, coherent and adherent film when spread on a surface and exposed to air. Normally, this process of oxidative polymerization is slow taking 12-36 hours. Various driers called siccatives, are, therefore, added to them to accelerate this process. Lead compounds have traditionally been popular as driers because they are cheap, easily available and the most effective. In addition, lead-treated paints, in presence of resins, transform the paint media into transparent gels that facilitate brushability. The lead-based driers are:

- (i) *Lead soap*: White lead is a chemically active pigment, and it reacts with both the free acidic portions of paints and the acids formed due to aging of paints. The reaction products are called '*lead soaps*'. These reinforce the paint films and stabilizes them.
- (ii) *Lead acetate*: This is also called '*sugar of lead*' and is the most popular as paint drier amongst all the metallic compounds. It enhances drying in damp weather.
- (iii) *Lead hydroxide*: This was used as a drier in the later part of the 19th century. But later on discontinued in favour of othe materials.

13. Type metals for hand-set printing: For this purpose, blocks of lead are melted to a semi-fluid state, and impressions of the type to be printed are taken on these blocks. Low melting point facilitates impression of the details. In this application, lead is alloyed with 2.5–25.0% Sb and 2.5–12.0% Sn. Antimony and tin help to reduce the melting point of the type metal to 238–246°C. Besides, antimony improves the hardness of the alloy.

14. Glass: Addition of metallic lead in the glass-making batch was first experimented with during the latter half of the seventeenth century, by an English scientist named George Ravenscroft. Since then, leaded glass is used when the glass is intended to be worked into intricate designs, and also when it is used in the optical industry for making superior quality and high-precision lenses. In this use, the properties of softness combined with malleability and high density of led are made use of. Due to softness and malleability, addition of lead increases the workability of glass. Similarly, due to high density, its addition increases the density and consequently, the refractive index of the glass. Thus the leaded glass performs better when used in the optical industry.

15. Miscellaneous alloys: Some of alloys used in specific applications have been mentioned under those uses. The other common alloys are :

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
"Ashtadhatu" or alloy of eight metals	Au, Ag, Cu, Pb, Sn, Fe, bronze and brass	This was first made during the prehistoric era, by mixing all the metals and their alloys that were known and available then. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship.
"Panchadhatu" or alloy of five metals	Alloy of Sn, Cu, Pb, Fe and brass	This is one of several types of "Panchadhatu" first made during the prehistoric era. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship. It is a cheaper version of "Ashtadhatu" sans gold and silver.

Contd....

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Pewter	Pb and Sn with addition of Sb	Antimony has a hardening effect. Old use dating back to Roman Era, in household articles.
Leaded aluminium alloys	8% Pb; 1% Cd; 1–4% S or Up to 10% Pb; 3–5% Cu; 0.5% Ni; 0.3–0.8% Mg or More than 10% Pb; small percentages of Cu, Mn, Zn, Fe and Si or More than 17.5% Pb	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.
Aluminium-copper-lead alloy	93.5% Al; 5.5% Cu and 0.5% Pb	Suitable for extruded bar sections amenable to be cut freely.
Brass	75% Cu; 21% Zn; 3% Pb; 1% Sn	Suitable for valves, pressure tight castings, plumbers' fittings, ornamental castings.
Leaded bronze	76% Cu; 9% Sn; 15% Pb; 2% Ni	Acid resistant bronze for use in poor lubricating conditions. Used in cranes and earth-moving equipment.
Tin-based white metal or Babbitt metal	88.25% (min) Sn; 3–4% Cu; 7–8% Sb; 0.5% Pb	Used in automobiles and engineering works.
Bearing metal	5–10% Sn; 10–15% Pb	Tin and lead alloy increase wear resistance.

16. Other uses: Lead-arsenate is used as an insecticide. Oxides of lead are used in processing of various products like glass, synthetic rubber, adhesives, glazes etc.

WASTE UTILIZATION

- 1. Recycling of scrap:** High resistance to corrosion makes lead metal products amenable to almost endless recycling. However, the lead used in tetraethyl lead, lead pigments and solders are permanently or irretrievably lost. On the other hand, the lead used in storage batteries, cable sheaths, roofing sheets, pipes and type metals can be easily recycled. Besides, dross formed as skums on molten lead during refining is also an important source of lead scrap. These scraps comprising lead dross are called 'rents' in trade circles.

The ratio of annually utilized quantities of scrap and the annual production of primary metal is called 'recycling rate'. According to an estimation made, the recycling rate of lead during 1992 was 59% in USA, 55% in Western Europe and 38% in Japan. The recycling of used storage batteries accounted for a major share in the production of secondary lead.

- 2. Sulphur recovery:** Theoretically galena (PbS) contains 86.6% lead and 13.4% S (cf., sulphur content in sphalerite 33% and that in chalcopyrite 35%). Due to this low content of sulphur in galena, serious thought has not been given to the question of recovering it unlike in case of copper and zinc ores. However, the sulphur in galena is driven off as SO₂ during smelting, and it adds to atmospheric pollution. So, environmental compulsion, if not economic compulsion, should make it worthwhile to make provisions for sulphur recovery in future lead smelters.

SUBSTITUTION

- 1. Anti-knocking:** Tetramethyl lead can substitute tetraethyl lead as an antiknock additive to gasoline. But the strongest objection to use of either tetraethyl lead or tetramethyl lead is that lead emissions are potential pollutant and hazardous to health. Benzene is used as an antiknock additive to lead-free gasoline. A new compound namely, methyl cyclopentadienyl manganese tricarbonyl or MMT is increasingly being recognized as a suitable lead-free substitute for this purpose.
- 2. Plumbing:** In water pipes, lead is now-a-days substituted by other less expensive but better materials like galvanized iron (GI), polythene etc. In brass, lead is added to improve machinability. But US and Canadian restrictions on lead content in potable water setting the limit at 15 ppb at the tap, have forced manufacturers to go for lead-free brass for use in potable water pipe line fittings. A new kind of brass called '*SeBiLOY*' was developed by replacing lead with selenium and bismuth. This alloy is now known as '*EnviroBrass*'. Depending on usage, its composition varies as: 4-38% Zn; 6%(Max) Sn; 0.5-2.2% Bi; 0.01-1.1% Se; 0.5% (Max) Fe; 0.25% (Max) Pb; 1.0% (Max) Ni; 0.25% (Max) Sb; 0.05% (Max) P; 0.6% (Max) Al; balance Cu. Selenium and bismuth contribute to machinability.
- 3. Construction:** In construction also, lead roofs have now given way to many new less expensive but superior materials like galvanized iron, asbestos, concrete etc.
- 4. Cable sheathing:** For sheathing of electricity transmission cables, PVC is used to substitute lead. In India, PVC sheathing was enforced for the first time in 1967-68 for up to 1.1 KV cables to start with. Subsequently it has been extended progressively to higher tension transmission cables. This has been necessitated by the deficiency in indigenous production of lead. Aluminium is also used to substitute lead in sheathing of such cables.
- 5. Paint:** In paint, red lead primer may be substituted by various non-lead primers like zinc chromate, barium potassium chromate and aluminium zinc oxide.

MAGNESIUM

Magnesium belongs to the trio of light metals — the other two being aluminium and titanium. More than 3% of the weight of our continents are estimated to be made up of magnesium oxide or magnesia (MgO), which is the basic ingredient of many igneous rocks. Magnesium constitutes 2.5% of the earth's crust. The metal is generally extracted from magnesia. The commonest source of magnesia is sea water, which contains 1.3 grams per litre of magnesium metal. Calcined dolomite (MgO.CaO), brines rich in magnesium chloride (MgCl₂), and salt wastes are other sources of this metal.

HISTORY

The bondage of magnesium (as well as the other two light metals) with oxygen is much stronger than that of the metals like copper, lead, zinc etc. This strong bondage was one of the reasons for magnesium remaining unknown to mankind till the modern times, unlike copper etc., which were smelted and reduced from their oxides millennia ago. Technology for reducing magnesium from its oxide was first invented and the metal— somewhat in impure state — isolated by Sir Humphrey Davy in 1808. In 1833, Michael Faraday prepared magnesium by electrolysis of fused anhydrous MgCl₂. The process was further developed by Robert Bunsen in 1852, which became the basis for its production on pilot plant scale in Germany in 1886. The process eventually advanced to commercial scale in 1909 in Germany, and this country monopolized the world market till the beginning of World War-I, i.e., 1915. Production began in USA in 1915, when the imports from Germany were cut off. Till the beginning of the World War-II (i.e., 1939), however, Germany continued to dominate the world market, and it was only after this war that USA began dominating the market. Other countries like Russia, Norway, Canada, Italy, Japan, France, UK etc. also began producing this metal in significant quantities.

The world production, which was only about 32000 tonnes in 1939 jumped to over 265000 tonnes in 1943. After the end of the World War-II in 1945, however, it was found that the peace time requirement of magnesium was much less than the needs during the war. As a result, the production slumped and in 1950, it was estimated to be merely 20000 tonnes (Excluding erstwhile USSR). But, the situation gradually changed since then, and the estimated world production of primary magnesium, in 2005, was about 600000 tonnes.

In India, production of magnesium metal started in a small way in 1970 when 560 kg was produced. After reaching a peak of about 107000 tonnes in 1977, it started declining and became irregular. The production during April 1990- March 1991 was about 49000 tonnes. During 2000, 2-3 plants were reported to be in existence, but figures of production have not been published.

RECOVERY

Magnesium metal is derived mostly from its oxide present in sea water. Originally, the magnesium oxide used to be derived by calcination of magnesite (MgCO_3). But, later on, sea water became the source material. The other sources of the metal are lake and well brines, wastes after extraction of salt, and calcined dolomite.

- (1) **Sea water:** Sea water, which contains 0.2 % MgO or 1.3 gm per litre magnesium metal, has been the major source of magnesium since 1937, replacing calcined magnesite. $\text{Mg}(\text{OH})_2$ is first precipitated by mixing sea water with $\text{Ca}(\text{OH})_2$, and then HCl acid is added by which a 15% MgCl_2 solution is yielded. This MgCl_2 -solution is concentrated by drying and is then electrolyzed to obtain magnesium metal.
- (2) **Brine:** Brine waters from certain lakes like Great Salt lake and Dead Sea are very rich in MgCl_2 , and can be directly electrolyzed to obtain magnesium metal.
- (3) **Salt waste:** The Central Electro-Chemical Research Institute, Karaikudi, India, after a sustained research starting in 1963, developed a process in 1986 to derive magnesium metal using the waste salt water route as against sea water. Sea water becomes saturated with NaCl at density 25.5°Be (equivalent to specific gravity 1.20). On progressive evaporation the density increases. When it reaches 30°Be (equivalent to specific gravity 1.26), most of the NaCl has precipitated and the wastes become rich in other salts including those of magnesium.
- (4) **Calcined dolomite:** Dolomite (double carbonate of calcium and magnesium) contains around 22% Mg. On calcination, the CO_2 is driven off leaving a mixture of the oxides of calcium and dolomite. Magnesium metal can be recovered from this calcined dolomite by silico-thermic process. In this process, a mixture of calcined dolomite and 75%-grade ferrosilicon is briquetted and heated in a retort. The magnesium oxide in the calcined dolomite is reduced by silicon, producing dicalcium silicate and magnesium vapour, which is condensed to crystals of 99.8% purity magnesium. These magnesium crystals are melted, refined and formed into ingots.

CRITERIA OF USE

- (1) **Specific gravity:** Magnesium having specific gravity 1.74, is an extremely light metal being $2/3^{\text{rd}}$ lighter than aluminium and $1/4^{\text{th}}$ lighter than steel.
- (2) **Workability:** The metal is ductile and amenable to cutting and machining with relative ease.
- (3) **Colour and lustre:** It is a silvery white metal with a good surface finish.
- (4) **Chemical affinity:** It has very strong bondage with oxygen and also affinity for other elements like hydrogen, chlorine, nitrogen etc.
- (5) **Thermal property:** Its melting point is 651°C . When ignited, it burns fiercely and combines with oxygen producing a brilliant white fire and crackling sparks. It has high thermal conductivity.

- (6) **Corrosion resistance:** Due to its affinity to oxygen, magnesium is generally not strongly resistant to corrosion, and it easily oxidizes in the presence of moisture.
- (7) **Nuclear property:** It has low neutron absorption and it is resistant to radiation damage.

USES

There are certain uses which are directly based on the natural minerals magnesite and dolomite. But these minerals are classified as industrial minerals, and not metallic ones. Hence, those uses will not be discussed in this book. The important uses of magnesium metal are:

- (1) Structural products
- (2) Alloys
- (3) Scavenger and de-oxidizer
- (4) Electro-plating
- (5) Powder metallurgy
- (6) Extraction of titanium dioxide by chlorination process
- (7) Hydrogen fuel system
- (8) Battery
- (9) Incendiaries and fire-crackers
- (10) Metal matrix composites (MMC)
- (11) Photographic flash light
- (12) Nuclear fuel element
- (13) Micronutrient

These uses are discussed as follows:

- (1) **Structural products:** In 1946 i.e., after the World War-II, when the demand of the military for magnesium slumped, its use as a structural metal began in USA primarily due to the unique combination of the properties of lightness and amenability to machining. But unlike aluminium, it cannot be used alone, and some alloying additive is necessary. In this application, it is used in the form of castings and wrought products (sheet, extrusions and forgings). The common methods of making magnesium-based structural components are by press-forging (or extrusion) and die-casting. In the press-forging method, the material is worked at around 400°C. The magnesium-based alloys a predominant content of magnesium (89% and above) that are used as structural materials are :

<i>Magnesium content (%)</i>	<i>Other elements</i>	<i>Uses</i>
96	2.5–3.5% Al; 0.7–1.3% Zn; 0.2% (min) Mn; 0.3% (max) Si	Sheet, plate, press-forgings, aircraft, guided missile parts, aircraft and car wheels.
92	5.8–7.2% Al; 0.4–1.5% Zn; 0.15% (min) Mn; 0.3% (max) Si.	Extruded bars and tubes, forgings.
90	5.3–6.7% Al; 2.5–3.5% Zn; 0.5% (max) Mn; 0.3% (max) Si; 0.1% Cu.	Sand-casting for use in aircraft and in machine parts for textile and packaging industries.

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<i>Magnesium content (%)</i>	<i>Other elements</i>	<i>Uses</i>
89	8.3–9.7% Al; 0.4–1.0% Zn; 0.13% (max) Mn; 0.5% (max) Si; 0.1% Cu.	Die-casting for use in pumps, portable tools etc. for operation under light pressure conditions.
93–97	2.5–6.5% Zn; 0.7% Zr	Called “ <i>ternary casting alloy</i> ”, very high stress resistance.
90	2.5–4.0% with Zn and Zr	Called “ <i>quaternary casting alloy</i> ”, remarkable resistance to creep at elevated temperatures.

The products include car components like door handles, carburetors, fuel pumps etc. In these, magnesium is being preferred to traditionally used zinc because of its lightness on account of which fuel efficiency can be achieved.

- (2) **Alloys:** These are the alloys which contain much less magnesium compared to structural materials. The king pin of most of the magnesium-containing alloys is aluminium. However, a few other alloys not containing aluminium are also produced. Due to the strong chemical affinity of magnesium – particularly in molten state, special care is taken during making of its alloys, to protect it against oxygen and nitrogen of the air. This can be done by using a flux consisting of a mixture of chlorides of magnesium, calcium, sodium and potassium, sometimes with addition of magnesium and calcium fluorides. Important alloys are:

<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(1) Aluminium-magnesium alloy with little silicon	50% Mg	Medium strength semis.
(2) Aluminium-copper-magnesium (Al-Cu-Mg)	—	Medium strength semis.
(3) Aluminium-zinc-magnesium (Al-Zn-Mg)	—	Combination of the properties of hardness and high strength midway between those of aluminium and ductile iron; cheaper alternative to bronze.
(4) Aluminium-zinc-silicon-nickel-magnesium	Si, Ni, Mg added in a matrix of Al-Zn	Used in light alloy crankcases of vehicle engines.
(5) Leaded aluminium alloys	Up to 10% Pb; 3–5% Cu; 0.5% Ni; 0.3–0.8% Mg	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.

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<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
(6) Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu ; Al-Si alloys containing 2–24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base	Used in self-lubricating bearings and other antifriction applications.
(7) Aluminium-mica alloy	Mica coated with Ni or Cu with addition of Mg	Good solid lubricant; can be used in bearings.
(8) Aluminium-magnesium-manganese	97.8% Al; 1.0% Mg and 1.2% Mn	Uses requiring high resistance to corrosion such as in roofing material.
(9) Aluminium-copper-magnesium-manganese	93.4% Al; 4.5% Cu; 1.5% Mg and 0.6% Mn	High strength with adequate workability; used in aircraft parts, truck wheels, etc.
(10) Aluminium-copper-silicon-magnesium	86.5% Al; 3.0% Cu; 9.5% Si; and 1.0% Mg	Casting alloys used in automotive pistons etc.
(11) Ferro-silico-magnesium	5–20% Mg	Spherodizing alloy.
(12) Ferro-silico-magnesium-titanium	—	Spherodizing alloy.
(13) Nickel-magnesium	15–17% Mg with or without cerium	Spherodizing alloy.
(14) Nickel-iron-magnesium	15–17% Mg; 15% Fe; balance Ni; with or without calcium	Spherodizing alloy.
(15) Ferro-magnesium briquette	15% Mg	Spherodizing alloy.

- (3) **Scavenger and de-oxidizer:** The strong affinity for oxygen makes magnesium suitable as a de-oxidizer in refining of metals. For the same reason, magnesium in the form of ribbon or wire is used to remove traces of gases from radio valves.
- (4) **Electro-plating:** Magnesium-plated surfaces have a bright bluish white finish. Magnesium-plating is achieved by precipitation of magnesium in an anodizing bath containing magnesium perchlorate or magnesium bromide through electrolysis.
- (5) **Powder metallurgy:** Powder metallurgy is the process whereby many small components are produced by fabricating metal powders or metal and ceramic powders together (for details see the chapter on Iron Ore - Hematite). Instead of by extrusion or die-casting, many magnesium products can be made by fabricating its powders through sintering, pressing etc.
- (6) **Extraction of titanium metal:** In the chloride process of titanium dioxide manufacturing, ilmenite or crude TiO_2 is chlorinated to produce FeCl_2 and titanium tetrachloride (TiCl_4).

For the purpose of producing titanium metal this TiCl_4 is treated with red-hot magnesium metal under an inert gas blanket (the inert gas is necessary because liquid titanium tends to absorb oxygen and nitrogen very rapidly and also magnesium has stronger affinity for oxygen than chlorine). The resultant products are commercially pure spongy titanium metal and MgCl_2 . The MgCl_2 is drained out and electrolyzed to recover both chlorine and magnesium for re-use.

- (7) **Hydrogen fuel system:** Liquid hydrogen has been used as a fuel for launching rockets. Now, intensive research is going on in Japan, Germany, USA and other countries to make it a suitable fuel for cars. Principal advantage of hydrogen fuel over that of petroleum lies in its practically zero pollution effect, the products of its burning being only heat and water. On the other hand, the most formidable problems are its low flash point that renders it highly inflammable and highly risky to carry in tanks. Now, research is directed to development of special alloys which will be able to absorb hydrogen and then slowly release it for combustion. It is in this context that magnesium has emerged as a possible answer due to its ability to absorb hydrogen.
- (8) **Battery:** Magnesium batteries have a magnesium anode, manganese dioxide cathode, and an aqueous solution of magnesium bromide or magnesium perchlorate. The main advantage of these batteries lie in their lightness and low cost. Hence they are used by army in portable electronic gadgets during training exercises, and in emergency locator beacon applications. Navy also uses them for mines. Their main disadvantage is that the magnesium chemicals used tend to emit toxic fumes when heated.
- (9) **Incendiaries and fire-crackers:** The intense white fire generated due to burning of magnesium in presence of oxygen has led its powder to be used as fillings of incendiary bombs that produce only fire, but not explosion. In such bombs, the casing is also made of an alloy of magnesium containing 5-7% aluminium.
- (10) **Metal matrix composites (MMCs):** A composite material is a materials system composed of a mixture of two or more materials deliberately combined to form heterogeneous structures with desired or intended properties. In composites, at least one of the constituents serves principally to strengthen or reinforce the composite, while another constituent, called the applications matrix, serves to confine the reinforcing constituent(s) and provides a means to distribute any applied stress. In metal matrix composites (MMCs), a metal serves as the matrix, while the reinforcing constituent can be a metal, a non-metal, an alloy or a compound. A metal matrix, namely *graphite-reinforced magnesium* is used for making tubes and fittings for space craft structural applications and rotary engines for propeller-driven aircraft.
- (11) **Photographic flash light:** This use was before the invention of multi-use electronic flash bulb. Ability of magnesium to burn instantaneously with an intensely white flash, made it suitable for use in photographic flash light powders. In practice, a fine-grained mixture of magnesium powder and potassium chlorate (or barium peroxide) used to be ignited by hand resulting in an intense flash of white light rich in blue ultraviolet light and harmless white smoke of magnesium oxide. Later on, single-use electronic flash bulbs contained magnesium filaments which were ignited electrically by a contact in the camera shutter. But these bulbs used to get too hot to handle with ease. It is still later when multi-use electronic

flash bulbs came to be used that magnesium lost its utility in this application. Such a bulb consists of a tube filled with xenon gas, and high voltage is generated by an electric arc producing a flash with duration as short as thousandth of a second.

- (12) **Nuclear fuel element:** In a nuclear reactor, the fuel element is a sort of container within which the fuel (*e.g.*, an isotope of uranium) is placed. The requirements that have to be fulfilled are that (i) the fuel element must not absorb the neutrons released within the fuel due to fission, (ii) it should not be damaged due to effects of radiation, and (iii) it should allow the heat generated due to nuclear fission to pass through for utilization in power generation. The low neutron absorption of magnesium along with its resistance to radiation damage and high thermal conductivity, makes it a suitable material for fabrication of fuel elements. Tendency of magnesium to oxidize and ignite is, however, a disadvantage. For this purpose, generally, magnesium is alloyed with beryllium. Addition of even 0.005% of beryllium reduces inflammability and oxidation.
- (13) **Micronutrient:** Magnesium is a necessary ingredient in human diet. It helps formation of healthy bones, manufacturing proteins, releasing energy from muscle and regulating body temperature. It enters the system of human body from soil through plants and vegetables.

MERCURY

Mercury, also known as '*quick silver*', was known to the Greek and the Chinese as early as 4th and 3rd centuries BC. its principal source is the mineral cinnabar (HgS). There are other economic minerals also, such as livingstonite (HgS.2Sb₂S₃) and metacinnabarite (HgS). Besides, the metal is found in native state in some ores. Mercury emissions from coal combustion are currently receiving attention both as an environmental hazard and as a source of mercury.

The metal is recovered by treating the sulphide at 700°C in a furnace. SO₂ is driven off and the mercury is separated in the form of vapour which, on cooling, yields the metal.

CRITERIA OF USE

Mercury is liquid at room temperature. While it solidifies at (-) 39°C, its boiling point is 357°C. Its specific gravity is high – 13.6. Its electrical conductivity is weak, being only 1.8% of that of copper. The metal and its chemical compounds are highly toxic. It can dissolve gold, silver and tin to form a kind of plastic alloys known as '*amalgams*' (the process of alloying with mercury is called '*amalgamation*'). When bombarded by high speed electrons, mercury atoms emit ultraviolet rays.

USES

1. **Thermometer:** Low melting point and comparatively low boiling point make mercury suitable for measuring temperatures up to about 300°C (cf., gallium at high-temperature ranges). It is widely used in clinical thermometers. However, mercury is not suitable for measuring very low temperatures below (-) 39°C which is its freezing temperature (for measuring still lower temperatures coloured alcohol is used).
2. **Barometer:** A barometer is a device for measuring atmospheric pressure. Liquidity at ordinary temperature and the high specific gravity are the key criteria in use of mercury in barometers. The average atmospheric pressure at sea level (1 atmosphere) can support a column of mercury 760 mm high (about 1 kg/cm² pressure is exerted by this column). The higher the atmospheric pressure, greater will be the height of this column. The unit of atmospheric pressure usually used in meteorology is the '*millibar*'. A mercury column of 750 mm corresponds to 1000 millibars.

3. **Thermionic rectifier:** Rectifiers allow current to flow in one direction only and also amplify the current output. The principle is related to electric emissivity. When voltage is applied, the electrons ejected from the hot cathode filament pass through a tube filled with mercury vapour. Initially, the flow of electrons is weak due to resistance of the vapour (electrical conductivity of mercury is weak). But on increasing the voltage, the electrons attain a very high velocity, and eventually, they ionize the mercury atoms on colliding with them. The electrical resistance of ionized gas being substantially lower, the flow of electrons suddenly increases and the power output from the rectifier tube becomes higher than the input power.
4. **Mercury vapour fluorescent lamp:** Such lamps are filled with mercury vapour at low pressure. When electrons are ejected from incandescent electrodes, they collide with mercury atoms, as a result of which invisible ultraviolet rays are emitted. These ultraviolet rays become visible rays upon hitting the inner surface of the lamp coated with some fluorescent substance.
5. **Dry cell:** Mercury had, in the past, been used in dry cells taking advantage of the lower position of mercuric oxide in the electromotive series with relation to zinc. Such cells were able to withstand temperature and humidity fluctuations, and were characterized by low-output and high self life. These cells consist of zinc anode, mercuric oxide cathode and an electrolyte of an aqueous potassium hydroxide. They were used for electrolytic preparation of chlorine and caustic soda.
6. **Metallurgy:** The ability of mercury to amalgamate with gold and silver has been harnessed in the recovery of these metals from their ores.
7. **Paints and pigments:** Various salts of mercury are used for these purposes. Mercuric oxide is used as a red paint in dry cell batteries, ships etc. The sulphide is a bright scarlet pigment and is used in printing inks.
8. **Medicines and insecticides:** Mercurous chloride (calomel) is a drug, while mercuric chloride is corrosive and is used as antiseptic, fungicide and insecticide.
9. **Mercury switch:** A mercury switch essentially consists of a glass bulb filled with some inert gas and containing a bead of liquid mercury. Two conducting filaments are moulded into it in such a way that they are not in contact with each other unless both are inside the mercury bead which thus completes the electrical circuit by virtue of its conductivity – albeit weak. Now, mercury bead being heavy flows freely down within the bulb when the latter is tilted. The filament ends are so positioned that when the mercury bead is at the centre, they will be inside it (circuit complete and switch is on), and when the mercury bead moves towards one end, either one or both of them will be out of the mercury (circuit broken and the switch is off). These switches are used to detect tilt motion such as in water level sensing and in vending machine alarms. In the former, when the level is perfect, the mercury bead will be at the centre and a light will be switched on. In the latter, when the vending machine is tilted or shaken by thieves, the rolling of the mercury bead in and out of the centre will put the switch alternately on and off and an alarm will ring. There are other applications also using this principle.
10. **Explosive detonator:** To make explosives safe to handle, they are made in such a way, that ordinarily they should be insensitive to heat, pressure etc. In other words, they should explode only when required, and this is achieved by using a detonator. A detonator

contains a small amount of explosive called '*priming explosive*' or '*primer*' or '*fulminating agent*', which is highly sensitive to heat, electric spark or friction. The small amount of such explosive can be handled safely with a little care. Mercury cyanate [Hg(ONC)₂] which is also called '*mercury fulminate*' is a highly sensitive explosive and it serves this purpose effectively in combination with acetylene and blasting gelatin. Mercury cyanate is made by dissolving mercury in nitric acid and then adding ethylene.

11. Other uses:

- (i) Mercury vapour boilers for power generation
- (ii) Plastic, dyestuff etc.
- (iii) Catalyst.

MOLYBDENUM

The incidence of the metal in the earth's crust is around 2 ppm. The most important ore of molybdenum is molybdenite (MoS_2). Theoretically, it contains 60% Mo. In nature, however, the deposits of this mineral contains very small quantities of MoS_2 – usually varying from 0.05% to less than 1 per cent. The economic cut-off grade of primary deposits is 0.25% as taken in USA, the largest producer. It is also found associated with some copper and uranium ores. Grades of even 0.02–0.08% MoS_2 is considered good enough in such secondary occurrences.

HISTORY

The name molybdenum comes from the Greek word “*molybdos*” meaning lead, probably because molybdenite was first identified, by a Swedish chemist named Karl Scheele in 1779, as a distinct mineral species in a sample which was more familiar as a lead-containing substance. The metal was later isolated by P.J. Hjelm in 1782. Though its commercial production started in 1893, during the initial years, the annual production was of the order of only one or two tonnes. Its potentiality as an industrial metal was, however, recognized in 1913 i.e., just before the World War-I, and production picked up well before the World War-II (1940–44), when steel containing molybdenum came to be used in artilleries by the Germans.

The average annual production of the metal during the 5-year period 1934–38 was over 10000 tonnes which increased to about 21500 tonnes in 1947. By 2001, it reached the level of 134000 tonnes.

There is practically no production of this metal in India, except some small quantities of MoS_2 concentrate produced occasionally as by product from uranium mine. But its intermediate product ferromolybdenum is being regularly produced since 1967 based mostly on imported concentrate.

RECOVERY

Molybdenum is recovered in three basic forms for industrial use as follows:

- (1) **Technical grade molybdic oxide:** Molybdenite ore is concentrated by froth flotation to produce a concentrate containing 75–90% MoS_2 (in case of primary ore) or about 55%

(in case of secondary ore). In the next step, the concentrate is roasted to yield a technical grade molybdic oxide (MoO_3) containing minimum 55% Mo.

- (2) **Ferromolybdenum:** This is manufactured from the technical grade oxide by thermite process. In this process, a mixture of molybdic oxide, aluminium, ferrosilicon, high grade iron ore and fluorspar is ignited. Ferromolybdenum settles below a layer of slag which is drained out. The ferromolybdenum is cooled, quenched and crushed. It contains a minimum of 55% molybdenum.
- (3) **Molybdenum metal:** This is obtained by first dissolving the molybdic oxide in NH_4OH solution to form ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$, which is then reduced with hydrogen. It is marketed in the forms of foil, wire, rod, mesh, powder, tube and sheet.

CRITERIA OF USE

- (1) **Hardness, strength and ductility:** Molybdenum is a very hard, strong and ductile metal. Its hardness is almost same as that of tungsten.
- (2) **Melting point:** Its melting point is very high at 2610°C . Amongst the metals, it is only next to tungsten which melts at 3382°C .
- (3) **Specific gravity:** It is heavy with specific gravity 10.22.
- (4) **Electrical conductivity:** Its electrical conductivity is similar to that of tungsten – 33% of standard copper i.e., International Annealed Copper Standard or IACS.
- (5) **Thermal expansion:** Being $5.35 \text{ ppm}/^\circ\text{C}$, its thermal expansion is higher than that of tungsten.
- (6) **Chemical reactivity:** It forms chemical compounds with elements like oxygen, silicon etc, but does not react with mercury. It oxidizes more readily than tungsten.
- (7) **Alloyability:** It can form alloys with various ferrous as well as non-ferrous metals.

USES

Principal Industrial uses of molybdenum are:

- (1) Alloys (ferrous and nonferrous)
- (2) Powder metallurgy
- (3) Electrical applications
- (4) Electronics
- (5) Nitrogen fixation
- (6) Chemicals (bearing material, catalyst, high temperature applications, fertilizers, pigments, analytical chemistry, lubricants).
- (1) **Alloys:** Role of molybdenum is mainly to improve the hardness, strength, ductility, and resistance to shock, fatigue and creep – particularly at high temperatures of $330\text{-}550^\circ\text{C}$. For alloying with iron and steel, it is added in the form ferromolybdenum, which combines with a part of the carbon present in pig iron or steel to form molybdenum carbide. The important alloys are as follows:

<i>Alloy</i>	<i>Composition</i>	<i>Functions/Uses</i>
(1) 1.5% manganese-molybdenum steel	0.35% C; 1.6% Mn; 0.25% Mo and the balance Fe	Crank shafts, connecting rods, axles, bolts and studs requiring high tensile strength.
(2) 1% chromium-molybdenum steel	0.4% C; 0.8% Mn; 0.9% Cr; 0.2% Mo and the balance Fe	General purpose bolts, motor axles, crank shafts etc. requiring high tensile strength.
(3) 3.25% nickel-chromium-molybdenum steel	0.3% C; 0.6% Mn; 2.5% Ni; 0.6% Cr; 0.6% Mo and the balance Fe	For withstanding severest of mechanical stresses and tempering as in axles and transmission shafts of trucks and tractors.
(4) Nitralloy steels	0.2–0.5% C; 0.35% Si; 0.65% Mn; 1.6% Cr; 1.1% Al; 0.2% Mo; balance nitrided steel	Surface-hardened steel which are machinable.
(5) Nickel-chrome-molybdenum case hardening steel	0.15% C; 0.5% Mn; 4.2% Ni; 1.2% Ni; 0.2% Mo and the balance Fe	Used where very high core strength is required, as in transmission gears and plastic moulding dyes.
(6) Nickel-free stainless steel	16–18%Cr, 0.95–1.20% C; 0.75% (max) Mo and the balance Fe	Fully hardenable, stainless steel.
(7) High-nickel stainless steel with added copper	18%Cr, 18% Ni, 0.07% C; 3.5% Mo; 0.6% Ti; 2.0% Cu	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (e.g., chemical equipment).
(8) Low-nickel stainless steel	16–18% Cr, 10–14% Ni, 0.08% (max) C; 2–3% Mo and the balance Fe	Superior corrosion resistance.
(9) Hadfield steel or austenitic manganese steel with added molybdenum	0.92–1.4% C; 12–14% Mn; 0.5–2.0% Mo and the balance Fe	High toughness and ductility with high work hardening capability and good abrasion resistance under impact; suitable in rails, earth-moving machinery, mining machinery including rock crushers, grinding mills, dredge buckets, power shovels, bucket teeth and pumps. Addition of Mo improves the toughness and resistance to cracking of castings.
(10) Acid resistant austenitic stainless steel	20% Cr; 34% Ni; 3.4%Cu; 2.5% Mo and the balance Fe	Highly resistant to action of sulphuric acid.
(11) Titanium aluminium molybdenum tin silicon alloy	87.5% Ti; 0.5% Si; Al, Mo and Sn each 4%	High strength alloy, used for highly stressed structural components in aircraft and structural engineering.

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<i>Alloy</i>	<i>Composition</i>	<i>Functions/Uses</i>
(12) Titanium aluminium molybdenum alpha-beta alloy	89% Ti; 7% Al; 4% Mo	Poor weldability, but higher strength at high temperature; shallow hardening.
(13) Austempered ductile iron (ADI) with added nickel and molybdenum	Steel with 1.5% Ni and 0.37% Mo	Steel with bainitic microstructure produced by special heat treatment (see "steel" under "Iron ore-hematite"). Substitute of ductile iron. unique combination of strength, ductility and wear-resistance. Usable in motor gears, tyre-cutting knife, truck shaft.
(14) Stellite	25–30% Cr; 1% (max) Mo; 2–15% W; 0.25–3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co	Used in hard facing materials (e.g. armaments, cutting tools).
(15) High resilience alloy	40% Co; 20% Cr; 15% Ni; 7% Mo 0.04% Be; balance Fe or 30% Ni; 8% W; 0.5% Be; balance Fe	Highly resilient, fatigue resistant, tarnish proof; suitable for watch spring.
(16) Surgical material	27% Co; 29.5% Cr; 36% Ni; 6% Mo; 1.5% Be	Excellent resistance to tarnish, and abrasion, compatibility with mouth tissues and body fluids, high strength, good casting properties, lower cost than precious metals. Used in dentistry and bone surgery.
(17) High strength and high corrosion resistance alloy	60% Ni; 15% Cr; 7% Mo; 0.6% Be; balance Fe	Surgical instruments.

(2) **Powder metallurgy:** *Powder metallurgy* is the process whereby many small components are produced by fabricating metal powders or metal and ceramic powders together (see "steel" under "Iron ore-hematite"). Molybdenum is amenable to this process.

(3) **Electrical applications:**

(a) *Electric bulb:* An electric bulb consists of a filament made of tungsten wire in the form of a coil welded to thicker support wires and encased in a glass bulb, the inside of which is either vacuum or filled with some inert gas to prevent oxidation during glowing. The current, when entering the thin filament from the thicker support wire, meets with high resistance due to reduction in the cross sectional area, and as a result it glows and emits light. The intensity of heat and light is directly proportional to the length of the filament in the coil. Molybdenum finds use in the thicker support wires, because its ductility and electrical conductivity are as good as those of tungsten, but

its fusion temperature, although very high, is lower than that of tungsten. Since there is no air or oxygen inside the bulb, the strong affinity of molybdenum for oxygen does not come in the way.

- (b) *Mercury switches*: Unlike tungsten, molybdenum oxidizes very readily and hence is not suitable for applications in electrical contacts in air. But, its ability to get readily wet by mercury without chemically reacting with the latter, makes it suitable in low-resistance contacts in mercury switches.
- (4) **Electronics**: Molybdenum, mainly due to its electrical conductivity, finds use in radio-receiving and – transmitting valves – usually alloyed with tungsten. Also, it is efficient in applications like bases of semiconductor devices, in which it is not exposed to oxygen.
- (5) **Nitrogen fixation**: Molybdenum has been found to be important in researches on *nitrogenase* – a molybdenum-containing enzyme, which is present in nitrogen-fixing bacteria (e.g., *Rhizobium*). These bacteria are used to help in the reduction of atmospheric nitrogen to ammonia, and in other applications involving nitrogen fixation.
- (6) **Chemicals**: Chemical affinity of molybdenum enables it to form compounds which possess varied properties suitable for different uses. The important molybdenum-based chemicals are as follows:
- (a) *Disilicide ($MoSi_2$)*: It is characterized by excellent resistance to oxidation even at high temperatures above 1300°C , making it suitable for some high temperature applications (e.g., ceramics).
- (b) *Oxide (MoO_3)*: It serves as a catalyst in industrial oxidation of the mixture of propane and ammonia for making propane-nitrile or acrylonitrile.
- (c) *Disulphide (MoS_2)*: Its crystal structure is lamellar, making it suitable as an additive to lubricants like oils, greases, aerosol sprays and nylon bearings (used in domestic appliances having poor lubrication facilities) required to function under high temperature and pressure conditions.
- (d) *Ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$* : It is a standard reagent in analytical chemistry for determination of phosphorus.
- (e) *Lead molybdate*: It is used as a pigment in ceramic glazes.

NICKEL

Nickel is a transition element exhibiting both ferrous and nonferrous metal properties, and is only second to manganese as a ferro-alloy metal, but it has other uses also. Its incidence in the earth's crust is 80 ppm, but it is believed to be a significant component of the earth's core. It has also been found in many meteorites. In fact, the naturally occurring alloy *kamacite* containing 90-95% Fe and 5-10% Ni is found in iron meteorites, and the nickel is considered as one of the criteria to distinguish a meteorite from other minerals. The ores primarily mined for nickel fall into two classes: (i) sulphides and (ii) silicates, and there are two types of commercial deposits namely, (i) magmatic sulphide and (ii) laterite.

Commercially the most important sulphide mineral is pentlandite [(NiFe)S], theoretically containing 36% S, 42% Fe and 22% Ni, and it occurs in primary deposits. In nature, it is associated with sulphide of copper, and deposits containing 1-2% Ni is considered economic. Nickel sulphide in association with cobalt, copper, manganese and iron, is also found in sea-bed nodules which are receiving attention worldwide, and research and development studies are underway.

The most important silicate ore is garnierite which is a hydrated silicate of magnesium and nickel. The primary mineral has a composition [2NiO.2MgO.3SiO₂.6H₂O], but in nature its composition is variable. Economically minable deposits generally comprise residual concentrations or laterites formed due to weathering of the ultrabasic rocks, and contain 1-4% Ni in the form of garnierite-bearing limonite or nickeliferous limonite.

There are other minerals like millerite [NiS], Niccolite [NiAs], nickeliferous pyrrhotite etc., but they are not of economic significance at present. Gersdorffite — a sulpharsenide of nickel (NiAs₂.NiS₂), which occurs along with lead-zinc ore in Bawdwin deposit in Myanmar, used to be processed for recovery of nickel until 1940.

HISTORY

Nickel, due to its nature of occurrence in association with copper, was mined as a combined ore with copper during prehistoric times. Bronze, found in Syria and dating 3500 BC has been found to contain 2% Ni. Some old Chinese manuscripts also point to knowledge of “*white copper*” (believed to be present nickel) during the period 1400-1700 BC. But those were not examples of conscious usage of nickel, and it went into copper alloys from the ores without being isolated. In around 1751, a mineral called “*Kupfernickel*” in German and meaning “*false copper*” or “*Devil's copper*” was being

widely used for colouring glass. In 1751, a Swedish chemist called Baron Axel Fredrik Cronstedt, who was trying to get copper from this mineral, isolated a new white metal. The metal was given the name nickel after Kupfernickel (later named niccolite after St. Nicholas). It is known to be used in 1843 in plating, but that was as a minor constituent in combination with other metals. The first coin of pure nickel was made in 1881. But its large scale industrial use as a distinct metal had to wait till 1905, when the nickel-copper alloy *monel* was invented and it formed the base for important commercial materials. It was only then that mining and processing of nickel as the main target metal received impetus. The world mine production (excluding erstwhile Soviet Union) in terms of the nickel metal contained in the ore, jumped from about 38000 tonnes in 1926 to 172000 tonnes in 1943 when the World War-II was at its peak, and then immediately after the war, in 1946, it slumped to about 114000 tonnes, rising again to about 180000 tonnes in 1953, i.e., during the Korean war. The annual production in all the countries taken together remained within the range 0.9-1.0 million tonnes during the period 1990-95, and marginally rose to 1.2 million tonnes in 2000. there is no production of primary nickel in India, and it is recovered in small quantities in the form of nickel sulphate as a byproduct from copper smelting.

RECOVERY

Nickel is extracted and marketed in the form of powder, strip, etc. Typical principles of its recovery of nickel from different types of ore are as follows:

1. Nickel-copper-iron sulphide ore:

- (i) If the nickel-content is not more than 2.5%, then the ore is first crushed, ground and concentrated by froth flotation; if the nickel-content is more than 2.5%, then these steps are not considered necessary.
- (ii) The concentrate or the high grade ore is roasted to drive off 50% of the sulphur, and to oxidize the iron.
- (iii) This roasted product is then smelted with a flux at 1200°C either in a blast furnace or an electric arc furnace, to obtain what is called “*furnace matte*”, which is blown with air to oxidize the remaining iron and another 25-30% of the sulphur.
- (iv) The iron oxide is separated out and the product after this operation is called “*Bessemer matte*”. It contains nickel, copper, cobalt and around 22% sulphur with a little precious metals.
- (v) The molten Bessemer matte is slowly cooled to get large crystals of copper sulphide, nickel sulphide, cobalt sulphide and precious metals. The precious metals are separated out magnetically after crushing and grinding the crystals.
- (vi) The main fraction consisting of the sulphides of copper and nickel are concentrated by flotation, and then smelted to separate nickel sulphide from copper sulphide to get impure metal containing 95% nickel and 5% cobalt and some precious metals.
- (vii) Through roasting and sintering, this impure nickel metal is converted to granular nickel oxide. Portion of this is directly marketed for making Fe-Ni alloy.
- (viii) The remaining NiO is reacted with water gas (mixture of CO and H₂) at 230°C ; the oxide first gets reduced by the hydrogen to an impure form of nickel metal, which then reacts with the CO to form nickel tetracarbonyl [Ni(CO)₄] gas.

- (ix) When this hot nickel tetracarbonyl gas is passed into a high temperature chamber containing spherical particles of metallic nickel in fast motion; the carbonyl quickly decomposes depositing metallic nickel on the spheres, and releasing CO gas which is re-circulated into the circuit.
- (x) Further purification of the nickel is done by electro-refining using sulphate-chlorate electrolyte, to get 99.5% pure nickel cathode and cobalt and precious metals as byproducts.
- 2. High grade lateritic ore:** A typical ore (New Caledonian ore) contains around 3% nickel with cobalt and iron, but not copper. The ore is smelted in blast furnace with coke and gypsum. The resultant *nickel matte* is electro-refined.
- 3. Low grade lateritic ore:** A typical ore (Cuban ore) contains 1.5% Ni with cobalt and iron. There are two processes:
- (i) *Pyro-metallurgical:* The ore is ground and reduced by producer gas at 700°C. Bulk of the iron is reduced to magnetite, and the nickel compound to metal. The mixture is leached with ammonium carbonate solution, which dissolves the nickel selectively as Ni-NH₄-carbonate solution. This solution is distilled to remove NH₃ and part CO₂, precipitating nickel carbonate, which is calcined to get nickel oxide. Then the rest of the process is the same as for sulphide ore.
- (ii) *Hydro-metallurgical:* Ore containing nickel and cobalt is dissolved selectively in sulphuric acid by pressure, separating out the iron. From the solution, sulphides of nickel and cobalt are precipitated by passing H₂S gas. The rest of the process is the same as for sulphide ore.
- 4. Low grade ore associated with ultramafic rocks:** For recovering nickel from low grade ore (0.8% Ni) occurring in weathered overburden of chromite bodies of Sukinda, India, the Regional Research Laboratory, Bhubaneswar has tested a process on pilot plant scale. The process involves reduction roasting followed by ammonia leaching and precipitation of basic nickel carbonate, followed by its dissolution using nickel-spent electrolyte, purification by solvent extraction, and finally electro-winning of nickel in the form of 99.0% pure nickel cathode.
- 5. Very low grade sulphide and lateritic ores:** In Western Australia, commercial breakthroughs have been reported in 2001, in high pressure acid leaching technology to treat nickel-bearing laterite deposits and bacterial leaching technology to process low grade nickel sulphide ore (it is claimed that in this process, the natural bacterial action is quickened 500000 times).

CRITERIA OF USE

- (1) Nickel is moderate in strength and hardness (3.8 on Mohs scale).
- (2) It is tough, but ductile and malleable.
- (3) Pure nickel is silvery white in colour, and has a lustrous shine.
- (4) Its specific gravity is 8.9.
- (5) Electrical conductivity of pure nickel is 25.2% of standard copper i.e., IACS or International Annealed Copper Standard, and 24% of that of silver.
- (6) It is electropositive in relation to hydrogen.

- (7) Its thermal conductivity is on the lower side, being only 15% of that of silver.
- (8) It melts at 1453°C.
- (9) It is moderately magnetic.
- (10) At ordinary temperature, it is inert to oxidation and resistant to corrosion. Hence, can retain its shine without tarnishing.
- (11) It is only moderately reactive and has good resistance to attacks by alkalis – even at high temperatures. It dissolves in dilute acids very slowly.
- (12) It is an excellent shield against electromagnetic radiation.
- (13) It has excellent ability to alloy with both ferrous and nonferrous metals.

USES

The important uses of nickel metal are:

- (1) Stainless steel
- (2) Coinage
- (3) Alloys
- (4) Nickel plating
- (5) Rechargeable batteries
- (6) Magnetic shield
- (7) Permanent magnets
- (8) Nickel-bearing tungsten carbide tools
- (9) White gold
- (10) superconductor
- (11) Catalyst
- (12) Chemicals
- (13) Electronics

(1) Stainless steel: Stainless steel is a special type of alloy, which has come to be regarded as a distinct commodity in trade and commerce. It may be defined as alloy steels containing more than 9% chromium – with or without other elements like nickel, manganese, selenium, molybdenum, titanium and niobium. It is characterized by a high degree of resistance to corrosion or oxidation or rusting. If nickel is added, then the stainless steel has resistance to corrosion at high temperatures superior to that containing only chromium. The stainless steel containing both chromium and nickel has austenitic structure and is relatively more workable. There may be different combinations of the two called *duplex* stainless steels. The products containing both chromium and nickel belong to the 300-series of the series of codes allotted by the American Iron and Steel Institute (AISI) to different stainless steels depending on the chromium- and nickel-contents (for more details, see “Stainless steel” under “Iron Ore—Hematite”).

Most of the nickel produced is used in making superior quality stainless steel. The chief criteria are its resistance to alkalis, acids and corrosion, and its malleability to facilitate fabrication. Besides, its silvery white colour contributes to attractive finish and appearance of the stainless steel object. Also, it is not too heavy to increase the weights of the objects (e.g., utensils, surgical instruments) much. The commonly traded and used varieties of nickel-based stainless steel are:

<i>Nickel content</i>	<i>Other elements</i>	<i>Properties/Uses</i>
18%	18% Cr; 0.07% C; 3.5% Mo; 0.6% Ti; 2.0% Cu.	Suitable for applications requiring strong resistance to chemical attacks by sulphuric and other acids, and sulphates and other salts (<i>e.g.</i> , chemical equipment).
19–22%	24–26% Cr; 0.08% (max) C	Uses requiring resistance to scale and stress at temperatures as high as 1000 ⁰ C (<i>e.g.</i> , staking equipment, furnace parts).
6–8%	16–18%Cr; 0.15%(max) C	Ferritic. Hardenable.
Low	(+) 20% Cr	Mixture of austenite and ferrite (duplex); can be strengthened by addition of nitrogen. Very high performance stainless steel, strong, with high corrosion resistance and very good weldability. Used in appliances, in nuclear stations, in fabrication of large diameter tubes, in coins.
8–12%	18–20% Cr; 0.8%(max) C	Astenitic; superior corrosion resistance.
8–12%	18–20%Cr; 0.03%(max) C	Resists formation of chromium carbide around crystal boundaries.
10–14%	16–18%Cr; 0.08%(max) C; 2–3% Mo	Superior corrosion resistance.
9–12%	17–19%Cr; 0.08% (max) C; 5-times carbon- content Ti	Resists formation of chromium carbide around crystal boundaries.
9–13%	17–19%Cr; 0.08%(max) C; 10-times carbon- content Nb	Resists formation of chromium carbide around crystal boundaries.

(2) Coinage: Nickel forms and integral component in most modern day coins. Earlier, in many countries like India, UK, silver and silver-based alloys were popular materials for coin-making. In 1940, 5% Ni started being added to silver coins in India, and in 1941, brass coins with 1% nickel added to brass (alloy of copper and zinc) were introduced. But since 1946, nickel-copper alloy has become a standard coin replacing silver coins. Such coins contain 25% Ni and the balance copper. In USA and Canada the 5-cent coin is popularly called as “nickel” contains 25% nickel. The high malleability makes it easy to work into flat-shaped coins. Also durability due to resistance to corrosion, acids and alkalis, and other criteria like attractive silvery colour, bright lasting shine and moderate specific gravity have made this alloy a cheaper alternative to silver coins.

(3) Alloys: An alloy is a metallic material consisting of atoms of two or more metals, or two or more elements of which most of the atoms are metal atoms. In an alloy, the elements are admixed at the atomic level, and bulk of properties are those usually associated with metals. Nickel is alloyed with ferrous and nonferrous metals to improve various properties like strength, toughness, hardness, corrosion-resistance etc. Over 3000 alloys containing nickel are known. Some of the alloys are predominantly nickel-based, and others nickel-bearing. The important amongst these are as follows:

- (a) *Monel metal*: This is the first conscious and commercial use of nickel dating back to 1905. It contains 66.0% Ni, 31.5% Cu, 1.35% Fe, 0.9% Mn and 0.12% C. Due to the predominance of nickel, its colour is almost silvery white and very attractive, and it is highly corrosion-resistant and hence durable, malleable and hence easily workable, and poorly magnetic. These properties make it useful in roofing sheets, shop fronts, food-cans, aircraft body parts, turbine blades, sinks, machine parts, chemical equipments, small fittings in marine craft etc.
- (b) *Cupro-nickels*: There are three varieties:
- 90/10 type cupro-nickel containing 88% Cu, 10% Ni, 1.5% Fe and 0.5% Mn; it is corrosion-resistant. It finds application in oil coolers, tubes for salt water condensers, fuse wires etc.
 - 70/30 type cupro-nickel containing 68% Cu, 30% Ni, and 1% each Fe and Mn; it is also corrosion-resistant as above, but more strongly; in addition, it has high tensile strength. It also finds application in oil coolers, tubes for salt water condensers for use in naval vessels, fuse wires etc.
 - Constantan containing 55% Cu and 45% Ni; it has practically zero temperature coefficient of resistance and it gives a thermal electromotive force (EMF) against copper. It finds application in thermocouples for use at temperatures up to 400°C, and also in precision rheostats.
- (c) *German silver or nickel silver*: This is not silver, and is an alloy containing mainly copper, nickel and zinc (in other words brass + nickel). It is called so because of its bright silvery appearance. There are three varieties:
- 10% nickel silver containing 62% Cu, 10% Ni and 28% Zn; it is used in the form of sheet and strip for production of cutlery, tableware and decorative articles.
 - 18% nickel silver containing 55% Cu, 18% Ni and 27% Zn; it is used for making springs and contacts in telecommunication equipment.
 - machinable quality nickel silver containing 46.5% Cu, 9.5% Ni, 41.25% Zn and 2.75% Pb; it has good machinability and can be machined into non-standard shapes for making various decorative objects.
- The so-called “*silver plate*” is in fact electroplated nickel silver (EPNS) i.e., nickel silver with an electro-deposited coating of pure silver.
- (d) *Nickel-chromium alloys*: These alloys are rich in nickel with chromium and other metals. Nickel and chromium readily dissolve. Such alloys are very highly resistant to corrosion, acids, alkalis and heat. Some of the grades possess good electrical resistivity, and some others are resistant to creep at high temperatures. There are five grades:
- Inconel containing 76% Ni, 15.8% Cr, 7.2% Fe, 0.2% Si, 0.1% Cu and 0.04% C; it is resistant to corrosion at high temperatures. It finds application in engineering goods for use in severely corrosive environment at high temperatures.
 - Incoloy containing 32% Ni, 20.5% Cr, 46% Fe, 0.3% Cu and 0.04% C; it resists oxidation, carburization, corrosion and sulphur attack at high temperatures.
 - Nimonic containing 58% Ni, 20% Cr, 17% Co, 2.5% Ti, 1.5% Al and 0.13% (max) C; it is creep resistant at temperatures up to 920°C. It is used in gas turbine blades and discs, hot-working tools.

- Nimocast containing 76% Ni, 19% Cr, 0.3% Mn, 0.3% Cu, 0.4% Ti, 0.3% Al, 1.5% Co and 0.1% C; it resists oxidation at temperatures up to 1100°C. it is a casting alloy.
- Nichrome with two sub-grades namely, (i) “*chronin*” containing 80% Ni and 20% Cr; and (ii) “*ferrochronin*” containing 60-65% Ni, 15-20% Cr and 25% Fe. Both possess high electrical resistivity and resistance to thermal shocks due to repeated heating and cooling. They are used in heating elements of electric furnaces, toasters, stoves etc. The former is suitable for use at temperatures up to 1150°C and the latter, up to 800°C.

(e) *Other alloys*: Nickel is a versatile metals, there is a host of alloys containing relatively minor amounts of this metal. The important ones are as follows:

(1) Aluminium-zinc-silicon-nickel-magnesium	Si, Ni, Mg added in a matrix of Al-Zn	Used in light alloy crankcases of vehicle engines.
(2) Low aluminium-tin	5.5–7.0% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium’s machinability with improved strength; used in bearings where very high anti-friction properties are not essential.
(3) High aluminium-tin	20–40% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium’s machinability with improved strength; used in bearings where very high anti-friction properties are essential.
(4) Leaded aluminium alloys	Up to 10% Pb; 3–5% Cu; 0.5% Ni; 0.3–0.8% Mg	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.
(5) Graphitic aluminium alloy	Up to 16% graphite with or without coating of Ni/Cu ; Al-Si alloys containing 2–24% Si, up to 7.5% Ni, 4% (max) Cu and up to 1% Mg employed as base	Used in self-lubricating bearings and other antifriction applications.
(6) Aluminium-mica alloy	Mica coated with Ni or Cu with addition of Mg	Good solid lubricant; can be used in bearings.
(7) High-duty aluminium bronze	79.5% Cu; 9.5% Al; 4.5% Fe; 5.5% Ni; 1% Mn	Superior corrosion resistance in marine conditions; also high wear resistance.
(8) Ternary copper-nickel-tin spinodal alloy	85% Cu; 9% Ni; 6% Sn <i>or</i> 77%Cu; 15% Ni; 8% Sn	“Spinode” is a Greek word meaning cusp. This alloy is made by controlled thermal treatment called spinodal decomposition resulting in uniform dispersions of nickel and tin in the copper matrix, and is characterized by high mechanical strength, high wear resistance and high corrosion resistance in sea water and acid environments. Used in high-productivity mould tooling for the plastic industry;

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(9) Manganin	86% Cu; 12% Mn; 2% Ni	high-performance bearings for aerospace and heavy duty mobile industrial equipment; and highly corrosion resistant components for undersea oil and gas exploration. It has high electrical resistance and its thermal electromotive force (EMF) against copper is practically nil. It is used in precision electrical instruments like potentiometers, resistance boxes etc.
(10) 3.25% nickel-chromium-molybdenum steel	0.3% C; 0.6% Mn; 2.5% Ni; 0.6% Cr; 0.6% Mo	For withstanding severest of mechanical stresses and tempering as in axles and transmission shafts of trucks and tractors.
(11) Nickel-chrome-molybdenum case hardening steel	0.15% C; 0.5% Mn; 4.2% Ni; 1.2% Cr; 0.2% Mo	Used where very high core strength is required, as in transmission gears and plastic moulding dyes.
(12) Hadfield steel or austenitic manganese steel with added nickel	0.92–1.4% C; 12–14% Mn; up to 4% Ni.	High toughness and ductility with high work hardening capability and good abrasion resistance under impact; suitable in rails, earth-moving machinery, mining machinery including rock crushers, grinding mills, dredge buckets, power shovels, bucket teeth and pumps. Addition of Ni stabilizes the austenite, and that of Al improves the abrasion resistance by reducing the tendency of carbon to form carbides as well as preventing the formation of martensite during quenching or deformation.
(13) Nitinol	Ni and Ti	Used to hold broken bones in position for setting; it is preferable to stainless steel which is not resilient enough to yield sustained pressure. When heated by body-heat, nitinol rods expand, but comes back to original position thus maintaining sustained compressive effect.
(14) Austempered ductile iron (ADI) with added nickel and molybdenum	Steel with 1.5% Ni and 0.37% Mo	Steel with bainitic microstructure produced by special heat treatment (see “steel” under “Iron ore-hematite”). Substitute of ductile iron. unique combination of strength, ductility and wear-resistance. Usable in motor gears, tyre-cutting knife, truck shaft.
(15) High temperature nickel-cobalt alloy	Ni and Co	Not yet commercially produced. It has potentiality for use in hypersonic aircrafts.

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(16) Stellite	25–30% Cr; 1% (max) Mo; 2–15% W; 0.25–3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co	Used in hard facing materials (<i>e.g.</i> , armaments, cutting tools).
(17) Nickel-magnesium	15–17% Mg; balance Ni with or without cerium	Spherodizing alloy.
(18) Nickel-iron-magnesium	15–17% Mg; 15% Fe; balance Ni; with or without calcium	Spherodizing alloy.
(19) High resilience alloy	40% Co; 20% Cr; 15% Ni; 7% Mo 0.04% Be; balance Fe or 30% Ni; 8% W; 0.5% Be; balance Fe	Highly resilient, fatigue resistant, tarnish proof; suitable for watch spring.
(20) Surgical material	27% Co; 29.5% Cr; 36% Ni; 6% Mo; 1.5% Be	Excellent resistance to tarnish, and abrasion, compatibility with mouth tissues and body fluids, high strength, good casting properties, lower cost than precious metals. Used in dentistry and bone surgery.
(21) High strength and high corrosion resistance alloy	60% Ni; 15% Cr; 7% Mo; 0.6% Be; balance Fe	Surgical instruments.
(22) High tensile strength alloy	98% Ni; 2% Be	Aircraft fuel pump, hypodermic needle, matrix for diamond drill bits.

(4) Nickel plating: Nickel-plating is achieved by precipitation of nickel in an anodizing bath containing an anodizing bath containing nickel sulphate solution, through electrolysis. The metal object to be plated serves as the cathode and the acid serves as the anode. When electric current is passed through the anode, nickel, being electropositive, its ions move towards the cathode *i.e.*, the metal object, and deposits on the surface as a coating. Thus the nickel-plated surface acquires the properties of nickel such as bright shining silvery white appearance, corrosion resistance and durability etc.

(5) Rechargeable batteries: A battery is a device that translates chemical energy into electricity. Rechargeable or secondary batteries contain active materials that are regenerated by charging, in contrast to primary ones in which the energy is exhausted as materials are consumed. Essentially, a battery contains a chemical and two electrodes. When it is used, chemicals near one of the electrodes begin a reaction that produces extra electrons, which constitute electric current. There are two types of nickel-based rechargeable battery as follows :

- (a) *Nickel-cadmium(Ni-Cd) battery:* These have a cadmium anode, a nickel oxyhydroxide cathode and an electrolyte of an aqueous solution of potassium hydroxide. Nickel accounts for 20-30% of the weight of a typical cell. These can function at low temperatures and can be recharged at high currents. Such batteries suffer from what is called “*memory effect*”.

This means that if a cell is recharged before it is fully discharged, the remaining charge gets registered as the bottom line, and every time the cell will stop functioning at that level of charge. Ni-Cd batteries are used in short duration switch tripping devices, engine starters, navigation systems, telecommunication back-up etc.

- (b) *Nickel-metal hydride (Ni-MH) battery*: These are of higher capacities than Ni-Cd batteries and do not suffer from memory effect. The cathode and the electrolyte are the same as in Ni-Cd batteries, but its anode is made of a metal hydride instead of cadmium. The metal in the hydride is actually an intermetallic alloy comprising a mixture of rare earth metals and titanium or of nickel, cobalt, manganese, aluminium or of vanadium, zirconium, nickel, titanium. These batteries are used in digital cameras, pagers, hand-held radios, walkie talkies, cellular phones, shavers, flashlights etc.

(6) Magnetic shield: Nickel is moderately magnetic, but *mu-metal* (also called *Permalloy*), which is an alloy containing 77% Ni, 15% Fe and the balance Mo and Cu, is highly ferromagnetic (ferromagnetic materials are either naturally magnetic or attracted to a magnetic field and may be easily magnetized.; these concentrate the magnetic flux by a factor of more than 10 compared to vacuum, the magnetic permeability of which is taken as the unit value). The permeability of mu-metal is 10000 times that of vacuum, and it is magnetized easily even if the external magnetic field strength is very low. Consequently it does not allow interference by stray magnetic fields, and within a suitably designed chamber made of cylinders of this alloy, the residual magnetic field strength is ultra-low (less than 5 milligauss). If any sensitive instrument is placed within such a chamber, it will be effectively shielded against interference due to earth's magnetic field. This property of mu-metal is made use of when it is used as shield to screen vacuum chambers for experiments with low-energy electrons, magnetic resonance equipment, magnetometers, magneto-encephalography, magneto-cardiography, photo-multipliers etc. against interference from earth's magnetic fields.

(7) Permanent magnets: Permanent or hard magnets, once magnetized, retain their magnetic field indefinitely even after the magnetizing field is withdrawn. Magnetic alloys made by powder methods have uniform flux density and fine grain structure. Nickel is a constituent in "*alnico*" — an alloy of aluminium (8%), nickel (14%), cobalt (25%) and iron (50%) with little copper, niobium, silicon and titanium, which is made by powder metallurgical techniques and used in permanent magnets. Its magnetic field strength is 1500 gauss i.e., 3000 times the earth's magnetic field. Besides, its curie point (i.e., the temperature above which a substance loses its magnetism) is the highest amongst all magnetic materials – 800°C. Such magnets are used in generators, motors, communication/acoustic equipment etc. (see also the chapter on rare earth metals).

(8) Nickel-bearing tungsten carbide tools: Tungsten carbide tools are produced by sintering (i.e., insipient fusion) a mixture of tungsten carbide and cobalt or nickel in dies of desired shapes. Such tools are highly resistant to wear and softening at high temperature. Hence they are suitable for use under high temperature operating conditions, as in drilling bits.

(9) White gold: Gold is too soft to be used in pure form for making jewellery, and it is usually mixed with certain other metals like silver, copper, zinc which do not modify the yellow colour of gold. In the 1920s, however, there was a craze in some western countries, for white alloys of gold, popularly called white gold, which is fashionable even now. Nickel is an additive in such gold.

(10) Superconductor: A superconductor is an electrical conductor that approaches zero loss of current during transmission. Superalloys of nickel (e.g., inconnel, cupro-nickels), when dipped in liquid helium, may become a potential superconductor. But this is in research stage.

(11) **Catalyst:** Finely divided nickel is used as catalysts in hydrogenation for conversion of vegetable oils into solid edible fats, for cracking of petroleum, for purification of coal gas, for synthesis of nitrates, ammonia and several organic compounds.

(12) **Chemicals:** Nickel sulphate (NiSO_4) solution is used as the bath in nickel-plating. Nickel oxyhydroxide is used as the cathode in nickel-cadmium battery. Nickel arsenide (NiAs) i.e., the naturally occurring mineral niccolite, has pale green colour, and is a traditional colouring material for glass. The oxide NiO , when dissolved in water, assumes emerald green colour, and is used as a colouring additive in ceramics.

(13) **Electronics:** Ductility and electrical conductivity enables nickel to be used as “*Smart wires*” in robotics and electronic circuits.

WASTE UTILIZATION

Nickel-bearing wastes are of two broad types – scrap and effluents.

- (1) **Scrap:** Bulk of the nickel produced is consumed in stainless steel in which nickel is the costliest component. The used stainless steel products are recyclable as scrap. Such recycled stainless steel scrap serves to effect savings on nickel.
- (2) **Effluents:** Significant quantities of nickel are lost in the waste streams from nickel-plating industries, which is the third most nickel-consuming industry after stainless steel and alloys. According to an estimate made in 1980, as much as 5000 tonnes of nickel was wasted annually in the plating industry in USA alone. About 4% of the nickel consumed goes in waste in the form of sludge, spent-wash and other solutions. There are two main approaches:
 - (a) *Concentrate return methods or recycling:* In these methods, the solution containing the metal is recycled to the process tank. Before recycling, it is necessary to concentrate and purify the discharge, because otherwise the contaminants will also go into the process. The techniques employed include evaporation, reverse osmosis, ultra-filtration, electro-dialysis and ion exchange.
 - (b) *Non-return or recovery methods:* In these methods, the metal is extracted from the effluent. They do not involve returning of the metal to the originating process. There are less chances of contamination of the plating bath solutions. The techniques include electrolytic recovery, ion exchange, chemical precipitation and hydrometallurgy (leaching followed by precipitation and crystallization).

All these methods have been receiving attention of the industries and research institutions worldwide.

SUBSTITUTION

- (1) **Stainless steel:** Nickel is a desirable component of high grade stainless steel, but at the same time it is scarce and costly. For this reason, there is now a growing trend to produce low-nickel or nickel-free stainless steel without compromising too much on the quality of high-nickel one. Manganese has emerged as a popular substitute of nickel – wholly or partially.
- (2) **White gold:** Some countries have banned use of nickel as an additive in white gold, because it has been found that 10-20% of population are allergic to nickel. They are so sensitive that they develop skin rash, asthma and even cancer of lung and nasal sinus, when in contact with or exposed to nickel continuously for a long time. Palladium is a substitute of nickel in this use.

NIBIUM (COLUMBIUM)

An English Chemist called Hatchett in 1801, succeeded in extracting a new metal out of a rock sample from Columbia (USA) which he named 'columbite' after Columbia. In 1844, another Scientist Rose examined the same metal and found it very similar to tantalum. Since tantalum had derived its name from the Greek mythological character Tantalus, this new metal was named by him as niobium after Niobe, the daughter of Tantalus. Till 1951 the dual nomenclature continued — columbium in USA and niobium in Europe. In 1951, the Nomenclature Committee of the International Union of Pure and Applied Chemistry recommended 'niobium' as the standard name. The American Chemical Society also accepted it.

Niobium (Nb) occurs in nature in the form of two commercially significant minerals, namely columbite [(Fe,Mn)Nb₂O₆] and pyrochlore [(Na,Ca)Nb₂O₆]. Tantalum is usually associated with niobium due to their similar ionic radii. The average incidence of niobium in the earth's crust is 24 ppm.

RECOVERY

Niobium and tantalum which occur together, are extracted together by first fusing the ore with caustic soda, and then treating the melt with hydrochloric acid to dissolve iron, manganese and other impurities and to precipitate tantaloniobic acid crystals. This tantaloniobic acid is dissolved in hydrofluoric acid. Potassium fluoride (KF) is added and as a result, selective precipitation of tantalum-potassium-fluoride and niobium-potassium-oxyfluoride takes place. The two compounds are then separated. The niobium compound is treated with alkali to obtain niobium oxide. Pure niobium metal can be obtained by reducing the niobium oxide with niobium carbide in vacuum.

CRITERIA OF USE

Niobium is a steel grey, lustrous metal about as hard as wrought iron and having density of 8.6 gms/cc. The important criteria of its use for various purposes are as follows:

- (1) **Melting point:** Its melting point is high, being 2468°C.
- (2) **Corrosion resistance:** It is highly corrosion resistant, being inert to all acids except hydrofluoric acid and only very slowly oxidizable in alkaline solution.
- (3) **Mechanical property:** It is very ductile and malleable.
- (4) **Thermal conductivity:** Its heat transfer co-efficient (i.e., the amount of heat transferred per unit time per unit area per unit temperature difference) is 3 times higher than zirconium and 2 times higher than titanium.

- (5) **Nuclear property:** It has a low cross-section capture ability for thermal neutrons.
- (6) **Electrical conductivity:** It has high electrical conductivity and exhibits low temperature superconductivity at temperatures up to 9.15K.
- (7) **Chemical affinity:** Niobium has stronger affinity for carbon than for chromium, but weaker affinity for it than for tungsten.

USES

- (1) **Alloy:** Niobium is used for alloying with iron, steel and also for making high temperature superalloys based on nickel and cobalt which are used in rocket nozzles, spacecraft and missiles. The high melting point and corrosion resistance of niobium are carried into such alloys.
- (2) **Stainless steel metallurgy:** Ferro-niobium acts as a stabilizer during manufacturing of stainless steel. Chromium is one of the important constituents in stainless steel which, inter alia, also contains some carbon. The chromium, introduced in the form of ferrochrome or chargechrome tends to combine with the carbon of the steel and the resultant chromium carbide is deposited as a film at the grain boundaries. This prevents chromium from penetrating into the grains and reacting, thus making some grains of chromium deficient. Niobium having stronger chemical affinity for carbon than chromium, combines with the latter to form niobium carbide, thus preempting the formation of chromium-carbide. However, in low carbon stainless steel containing not more than 0.03% carbon, the addition of ferroniobium is not essential.
- (3) **Cutting tools:** Niobium carbide is used as a carbon provider to tungsten in the manufacture of tungsten carbide cutting tools. The affinity for carbon being weaker in case of niobium than in case of tungsten, the latter readily reacts with the carbon. Then the niobium serves to improve the corrosion resistance of the tool.
- (4) **Nuclear fuel element:** The fuel element in nuclear power reactors serves the function of a container or matrix within which the nuclear fuel is placed. The fuel element should not absorb the neutrons liberated in the fuel while at the same time it should transfer maximum quantity of the heat generated, because this heat is ultimately utilized for generation of steam to move the turbines. The twin criteria of low neutron capture and high heat transfer co-efficient make niobium a suitable material for this application.
- (5) **Superconductivity devices:** Because of its strong electrical conductivity and ductility, niobium is alloyed with titanium or tin to make superconductor wires. The alloy of niobium (3 parts) and tin (1 part) exhibit superconductivity up to 18.45 K.
- (6) **Other Uses:**
 - (i) Niobium metal finds application in vacuum tubes, high pressure sodium vapour lamps and catalysts.
 - (ii) Niobium pentoxide (Nb_2O_5) is used for making high quality optical glass and ceramics and also as transducer additive in piezoelectric systems. (piezoelectricity is the phenomenon of generation of electric charge by application of mechanical force and vice-versa. Certain substances like quartz show piezoelectric effect. When alternate compressive and tensile strains are applied, opposite electric charges will be generated. Transducer is a device by means of which energy can flow from one transmission system to another).
 - (iii) Niobium powder have become an important material in the prosthetic field.

PLATINUM GROUP METALS

The platinum group metals (PGM) comprises six metals namely, platinum, iridium, osmium, rhodium and ruthenium. These metals practically always occur in nature together in the form of a natural alloy, and they share many common attributes. All of them are extremely rare, all of them occur in mainly native state (although arsenides, sulphides and antimonides of these metals are also found associated with Cu-Ni sulphide types of deposits) and all of them are characterized by certain similar physical properties and similar industrial use.

It is not known when platinum was first discovered. Meteorites contain platinum and the earliest recorded meteorite impact on the earth happened two billion years ago. The Europeans knew about it in the early eighteenth century, and its use in ornaments was known to Columbian aborigines much earlier. The name platinum is derived from the Spanish word “platina” meaning ‘*little silver*’. These metals occur in some primary deposits associated with nickel, copper iron, chromium or gold. Sadbury deposit of Canada in one such important deposit. These metals are also frequently in alluvial placers in association with gold. A minimum tenor of about 0.75 gm/tonne of these metals in ore is considered economical to recover as byproducts. From the point of view of consumption, platinum and palladium are more important than the other metals of this group. World production of all the metals of this group during 2000 was 450 tonnes. Russia is the main producer of this group of metals in the world. There is no production of these metals in India.

CRITERIA OF USE

- 1. Refractoriness:** The metals of this group are highly refractory having high melting points as follows:

Osmium	: 2700°C
Iridium	: 2454°C
Ruthenium	: 2450°C
Rhodium	: 1966°C
Platinum	: 1773°C
Palladium	: 1554°C

- 2. Ductility:** Tensile strength of platinum and palladium is very high – 20700 psi and 30000 psi respectively. In general, all these metals are very ductile.

3. **Hardness:** Hardness of platinum is 4 to 4.5, and that of iridium and osmium ranges from 6-7 in Mohs scale.
4. **Malleability :** All these metals are valued for their easy workability. Particularly, palladium and rhodium are highly malleable and can be beaten up to the foils in the same manner as gold and silver.
5. **Chemical resistance:** All these metals are extremely resistant to tarnish and to practically all the chemicals. They are almost insoluble in all the acids. This resistance is sustained even at high temperatures.
6. **Colour and lustre :** All platinum group metals – more particularly rhodium – are white and lustrous metals having high reflectivity.
7. **Adsorption:** Palladium has a remarkable power of adsorbing gases – particularly hydrogen. In spongy form, it can adsorb 900 times its own volume of hydrogen. Also rhodium, platinum and palladium can adsorb oxygen efficiently.
8. **Electrical conductivity:** All these metals are good conductors. Expressed in terms of IACS or percentage of conductivity of standard copper, conductivities of these metals are: rhodium 38.40; ruthenium 22.70; osmium 18.20; platinum 16.28; palladium 16.00.
9. **Alloying ability:** The metals of this group are naturally alloyable with each other so much so that they mostly occur in nature in the form of a natural alloy. Besides, platinum can be easily alloyed with gold.
10. **Rarity:** These metals are extremely rare and hence, highly valuable.
11. **Magnetic property:** palladium is highly nonmagnetizable.

USES

1. **Jewellery:** Silver is the least expensive of the noble metals, gold has become overused for too long and too many people have been wearing gold jewellery, and now platinum jewellery has become the fashion and status symbol amongst the rich women in some countries like Japan. China has been the main centre of fabricating platinum jewellery. Colour, lustre, ductility, malleability, hardness, chemical resistance and rarity have all together contributed to this trend. The white colour is not just brilliant and attractive, but also regarded as a symbol of purity. While platinum is the most sought after metal for this purpose, palladium is also used as a substitute for platinum, whenever its price in the international market comes down relative to platinum. In this application, the metals used are of 95% purity.
2. **Spinnerets and nozzles:** In the viscose process of manufacturing rayon fibres, the viscose spinning solution of cellulose (chemically processed wood, straw, cloth pieces etc.) in caustic soda is pumped through spinning nozzles dipped in a bath of sulphuric acid, and coagulated cellulose emerges out of the nozzles in the form of fine filaments. In keeping with the fine diameter of the filaments, each nozzle is provided with a large number (up to 150 or so) of very fine holes (less than 0.1 mm diameter). These holes are called '*spinnerets*', and dimensional stability of these holes during repeated use over a long duration of time is essential for production of consistently high quality rayon. It is in these spinnerets that platinum group metal find use. Gold-platinum and platinum-rhodium alloys are mainly used.

Similarly, in the manufacture of fibre glass also, viscose solution of glass is passed through holes in nozzles and then drawn into fibres. Here also, platinum is used in making the holes.

Resistance of the metals to chemicals (including acids) and to wear and tear (due to hardness) are the key factors in these uses. Advantage is taken of the easy alloyability of platinum with both gold and rhodium for increasing hardness and chemical resistance of the material used.

3. **Electrical application:** Electrical conductivity and high melting point make platinum group metals suitable in heavy duty spark plugs required to perform consistently for very long periods of time without fouling, such as in military equipments. Similarly, in the contacts of heavy duty telephone relays, magnetos, voltage regulators etc., these metals find use. Platinum and palladium are mostly used.
4. **Electroplating:** The whiteness and high reflectivity make these metals suitable for plating on (i) silver wares to render high quality finish, and (ii) mirrors for search lights to improve reflectivity. Rhodium is the most preferred metal in these applications.
5. **Furnace:** Due to high melting point, platinum may be used in furnace elements for operations at high temperatures up to 1600°C.
6. **Hydrogenation:** Capacity to adsorb hydrogen and other gases make it an excellent catalyst – particularly in reactions involving hydrogenation and dehydrogenation.
7. **Surgical instruments and surgery:** Their hardness make the metals useful for manufacturing hypodermic needles, dental plates etc. Since iridium is harder than other metals of this group, it is alloyed with platinum and palladium for this application. In interventional radiology, platinum coils — as small as 2 mm in diameter—is used to cure aneurysm (cerebral stroke and hemorrhage). First, a catheter containing a microcatheter is pushed through the femoral artery in the groin, all the way to the brain. Platinum coils are introduced through the microcatheter into the aneurysm. The body's defences form a clot around the coils, reinforcing the area, in most cases sealing on the aneurysm and preventing further bleeding. These platinum coils can also be coated with hydrogels which swell up to nine times their volume when in contact with water of blood, and thus seal the aneurysm more effectively.
8. **Laboratory wares:** Strong chemical resistance and high refractoriness make platinum essential in manufacture of special types of crucibles for working with chemicals.
9. **Space craft:** In space craft fuels what is called '*cold combustion technology*' is employed. In this technology, hydrogen is ionized into ions and electrons. The liberated electrons flow through a circuit in the form of electric current which drives the motor. Here, platinum is used as a catalyst to facilitate ionization of hydrogen gas.
10. **Electrode boring:** This is a technique of making very fine bores (diameter may be as small as 0.004 mm). In conventional electrode boring, a fine platinum wire electrode is inserted within a glass tube, and positive and negative electrical charges from a DC source are applied to the object to be bored and to the electrode tube respectively. Due to flow of electrons, molecules of the object are eroded at the point of its contact with the platinum wire.

- 11. Catalytic converter:** Catalytic converters incorporated in petrol and diesel cars are a very important consumers of platinum, palladium and rhodium. These converters have become practically indispensable for controlling automotive pollution. A catalytic converter basically consists of thin sheets of ceramic, steel or steel-aluminium alloy which are assembled together in a honeycomb-like structure (to allow passage of exhaust gases freely through the openings) and which are coated with platinum (or palladium depending on their relative prices in the international market), rhodium and rare earth metals (sometimes all the three platinum group metals are also used). The whole assembly is enclosed in a steel case and fitted where the exhaust gases enter the silencer. The converter essentially functions on the principle of ion exchange. Rhodium catalyzes dissociation of the pollutant nitric oxides into environment-friendly nitrogen and oxygen. The next catalyst *i.e.*, platinum or palladium tackles the mixture of hydrocarbons and carbon monoxide by reacting first with the oxygen, then breaking up the hydrocarbon into hydrogen and carbon, and finally releasing the held-up oxygen to react with both hydrogen and carbon to convert them to water and carbon dioxide.
- 12. Commercial gold:** Gold is not used in its purest state, for fabricating jewellery because of its softness, and some other metals are alloyed with for hardening. Iridium and ruthenium are two metals commonly used for adulterating gold.
- 13. Standard kilogram and standard meter:** The unit for measuring mass based on a small cylinder of platinum-iridium alloy tucked away in a vault in Paris, has remained unchanged since 1791. The mass of this body was arbitrarily decided to be a kilogram and was accepted as the universal standard. Chemical resistance even at high temperature and resultant indestructibility was the criteria for choice of these metals. Similarly, standard meter is a rod of platinum, arbitrarily taken as the length of one meter.
- 14. Palladium plating of nonconducting surfaces:** For plating nonconducting surfaces (e.g., plastic), conventional process involving colloidal deposition of palladium is not feasible. So, first the surface is pretreated through precipitation of an adsorbing metal oxide like MnO_2 or Fe_2O_3 on the surface followed by treating the surface with transition metal ions like those of tin. Then the surface is treated with a solution of palladium ions. Palladium catalyzes chemical plating. The transition metal ions reduce the catalytic palladium ions into catalytic metal.
- 15. Other uses:**

 - (i) *Fountain pen nibs:* Osmium is used on account of its hardness (next only to iridium in this group) and resistance to corrosion by ink.
 - (ii) *Bearings of watches and compasses:* Osmium is used due to its hardness.
 - (iii) *Watch spring:* Due to nonmagnetizability, palladium is used in watch springs.
 - (iv) *Fine wires:* High ductility makes it possible to make very thin wires of platinum. Additional properties of high melting point and chemical resistance make these wires suitable in various laboratory experimental works.

(v) *Alloys:*

<i>Alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Titanium palladium alloy	Ti 99%; Pd 1%	Addition of small amounts of palladium improves resistance to non-oxidizing acids. Used in chemical industry.
Ruthenium alloyed with platinum group metals	—	Ruthenium serves to increase hardness.

(vi) *Catalyst:* Zeolite-based catalysts containing palladium is used as a catalyst in petroleum refining.

WASTE UTILIZATION

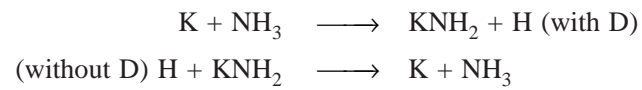
Recovery of platinum, palladium and rhodium from the used catalytic converters is an established practice – particularly in Europe and Japan. The process takes advantage of the unique properties of cyanide to selectively dissolve these metals from converters whereby a concentrate is obtained. The concentrate is then refined to recover pure palladium, platinum and rhodium. The technology can be adapted to treatment of zeolite-based catalysts used in petroleum industry.

POTASSIUM

Potassium is a soft and unstable metal. If in contact with air, it rapidly oxidizes. It is produced by thermal reduction of potassium fluoride (KF) by calcium carbide (CaC_2). It has strong affinity for chlorine, and this was the reason F. Wholer of Germany used it in 1828 for isolating beryllium metal by fusing it with this metal. But now it has only a couple of important uses as follows.

- 1. Coolant in nuclear reactor:** For transferring heat generated within fuel elements in a nuclear reactor, coolants are used. One of the coolant materials is the alloy Na-K, the advantage being that this alloy remains partly liquid even at room temperature.
- 2. Heavy water manufacturing:** Heavy water is deuterium oxide (D_2O), deuterium (D) being an isotope of hydrogen containing a neutron in addition to the proton of the latter. Deuterium occurs in natural water in one part for every 6000-7000 parts of hydrogen. Specific gravity of heavy water is about 10% more than that of ordinary water. Heavy water is used both as a moderator (for regulating the rate of emission or speed of neutrons during the chain reaction) and coolant in a nuclear reactor.

For manufacturing heavy water, there are various processes. One of them is water-ammonia exchange process, in which the role of potassium metal is as a catalyst. In this process the source of deuterium is ordinary water, and the differential affinity between deuterium and hydrogen with other substances is made use of. When ammonia is passed through this water at proper temperature-pressure conditions so as to prevent formation of its hydroxide, it picks up deuterium in preference to hydrogen. Then this deuterium-bearing ammonia is reacted with potassium to form potassium amide and giving off hydrogen which also contains the deuterium. The two are separated using their differential physical properties, and the deuterium is recovered while the hydrogen goes back to potassium amide to form ammonia leaving the potassium. The basic principles involved can be depicted in a simple way thus:



Both the ammonia and the potassium are reused and the process is repeated.

- 3. Micronutrient:** Potassium aids the synthesis of starch and sugar in all plants. It also helps plants withstand disease and harsh weather. For humans, potassium assists in muscle contraction and in maintaining fluid and electrolyte balance in body cells. It is also very important in sending nerve impulses, as well as releasing energy from proteins, fats and carbohydrates.

RARE EARTH METALS

The name 'rare earth' (RE in short) appears to be a misnomer. The name was given to a group of elements when they were discovered in early nineteenth century. The oxides of these elements resembled common earth which is a mixture of oxides of calcium, magnesium and aluminium, and at that time they were thought to be rare. Later on, some more closely related metals were discovered and were incorporated in the same group. In reality, however, these metals by themselves are not rare inasmuch as the incidence of some of them in the earth's crust is more than some common metals like lead, mercury, tin and platinum. They are called 'rare earth', because they do not fit neatly into the Periodic Table, and perhaps also because they rarely occur independently in concentrated quantities due to their strong affinity with other ore-forming elements with which they are always found associated.

A total of 17 metals are grouped under the term 'rare earth'. These are:

- (1) Scandium (Sc)
- (2) Yttrium (Y), and
- (3) 15 lanthanides, namely
 - (i) Lanthanum (La)
 - (ii) Cerium (Ce)
 - (iii) Praseodymium (Pr)
 - (iv) Neodymium (Nd)
 - (v) Promethium (Pm)
 - (vi) Samarium (Sm)
 - (vii) Europium (Eu)
 - (viii) Gadolinium (Gd)
 - (ix) Terbium (Tb)
 - (x) Dysprosium (Dy)
 - (xi) Holmium (Ho)
 - (xii) Erbium (Er)
 - (xiii) Thulium (Tm)

(xiv) Ytterbium (Yb)

(xv) Lutetium (Lu)

In the 1940s and 1950s, in some quarters, scandium and yttrium and in some others, lanthanum also, were not considered as members of this group. But this grouping of 17 metals has, by and large, found universal acceptance due to (i) their similarity in properties and (ii) the fact that they are always found together in nature.

These metals have also been classified into 'light cerium subgroup', 'heavy yttrium subgroup' and 'others'. The light group comprises eight of the metals with atomic numbers ranging from 57 to 64 and they are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium and gadolinium. The heavy group comprises another seven metals with atomic numbers ranging from 65 to 71, which are terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Since the remaining two metals namely scandium (atomic no. 21) and yttrium (atomic no. 39) were not originally included in the group of rare metals, they have not found place in either of the two subgroups.

The names of these metals have been derived as follows: scandium after Scandinavia; yttrium, ytterbium, erbium and terbium after the Swedish village Ytterby; europium after Europe; holmium after Stockholm; lutetium after Lutetis, the old name of Paris; thulium after Thule, the old name of Scandinavia; samarium after the Russian miner Samarki; cerium after the asteroid Ceres; praseodymium and neodymium after the Greek word 'didymium' meaning 'twin element'; lanthanum after a Greek word meaning 'to lie hidden'; and dysprosium after another Greek word meaning 'difficult to access'.

RECOVERY

The common sources of the rare earth metals are monazite [(Ce,Y)PO₄; contains 69.73% rare earth oxides], bastnasite [CeFCO₃; contains 74.81% rare earth oxides] and xenotime [YPO₄; contains 67% rare earth metal oxide]. In reality, however, the contents are lower. There is only one deposit of a pure gadolinium mineral – gadolinite – in Canada. Besides, these metals are also recovered as byproducts from some deposits of apatite [(Ca,Ce)₅(P,Si)O₄(O,F)], braunerite [(U,Ca,Fe,Y,Th)₃(Ti,Si)₅O₁₆] and euxenite [(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)₂O₆]. The broad principles involved in the recovery processes are as follows:

1. **Concentration:** The source mineral is first concentrated by combinations of flotation, acid leaching and calcination processes. The degrees of concentration of RE oxides vary depending on the feed mineral and the grade. Monazite concentrate may contain 55-65% RE oxide, bastnasite concentrate up to 85% RE oxide, xenotime concentrate up to almost 100% RE oxide.
2. **Separation of mixed RE oxide from non-RE:** The mixed rare earth oxide is separated by first precipitating with oxalate and then igniting the precipitate. Further concentration of the mixed rare earth oxide is effected by ion exchange methods.
3. **Recovery of mixed RE metals:** The mixed rare earth oxide is converted to chloride, and after adding some flux like CaCl₂, MgCl₂ or NaCl, is electrolyzed to obtain a mixed rare earth metal known as '*mischmetall*'. The separation can also be achieved by reverse osmosis using cellulose acetate membrane. In many of the commercial uses of rare earths, the mixed oxide, mixed salts and mischmetall serve the purpose, and the costly and tedious process of separation of individual metals in high purity is not necessary.

4. **Recovery of individual RE metals:** For obtaining cerium and lanthanum, repeated fractionation is done. For obtaining the other metals, either liquid-liquid extraction processes or (for highly purified metal products) ion exchange processes are practised.

CRITERIA OF USE

1. **Optical properties:** Some of the rare earth metals possess low dispersion, low emissivity and consistency in emissivity of different colours of light. Refractive index of some of the metals is high.
2. **Colour:** Colours of some of the metals are as follows:
 - Cerium : iron gray
 - Yttrium : reddish orange
 - Neodymium : red to light violet
 - Praseodymium : yellow to green
3. **Abrasive hardness:** Rare earth metals and their compounds are soft.
4. **Incandescence:** Oxides of some of the metals, when heated, give off an intense white light resembling sunlight.
5. **Light absorption:** These metals have ability to absorb ultraviolet rays, infrared rays and also the intense sodium-D light.
6. **Fluorescence:** This is the property by which a substance (also called '*phosphor*') transforms an invisible light radiation (*e.g.*, ultraviolet rays) into visible light with corresponding amplification. Different substances produce different colours of light. Cerium produces yellow green colour, while yttrium and europium produce intense red light.
7. **Chemical affinity:** Some of the rare earth metals have a strong affinity for the nonmetallic elements like hydrogen, carbon, oxygen, sulphur, phosphorus, nitrogen and the halogens.
8. **Alloying ability:** These metals can alloy with other metals.
9. **Energy transmission:** These metals are able to transmit short wave energy with low energy losses.
10. **Magnetism:** Naturally magnetic.
11. **Melting point:** Their melting points vary from 800-900°C.
12. **Neutron absorption:** Good ability to absorb neutrons.

USES

Though the rare earth metals hold great potentiality in usefulness, the use of some of them has not yet been fully established – particularly in the high-tech area of application. The common uses of the rare earth metals and compounds (particularly the oxides) are as follows:

1. **Glass:** The colours, abrasive hardness, optical properties and ability to absorb ultraviolet and sodium-D light rays are the principal criteria in this application. The main uses are described here.
 - (a) *Colouring:* Cerium, yttrium, neodymium and praseodymium are used for imparting colours ranging from neutral gray to yellow, red, violet, green etc. Carbonates of neodymium and praseodymium and cerium dioxide can be used for decolorizing

glass. Melting points comparable with other raw materials of glass, facilitate their addition during glass manufacturing also.

- (b) *Polishing*: Cerium oxide – either alone or mixed with other rare earth oxides, serves as a polishing agent for plate glass, television screen, lenses, mirrors etc.
 - (c) *Optical glass*: Due to low emissivity, and consistency in emissivity of different colours, high refractive index and low dispersion, lanthanum and its oxides are used as additives in the manufacturing of eye glasses and lenses of cameras, binoculars, telescopes etc.
 - (d) *Filter glass*: Cerium oxide absorbs ultraviolet rays and it is used in haze filter glass of cameras – specially for serial photography. Samarium can be used in infrared-absorbing glasses. Oxides of neodymium, erbium and praseodymium are used in television filters.
 - (e) *Goggles*: oxides of neodymium, praseodymium and cerium absorb the intense yellow light of sodium-D band. For this reason, these are used in goggles worn by glass blowers who are vulnerable to exposure to sodium excitation.
 - (f) *Cathode ray tubes*: Terbium, yttrium and europium are used in coloured cathode ray tubes of televisions and computers.
 - (g) *Colored lamps*: Europium, terbium and yttrium are used.
2. **Ceramics**: Mixed oxides of rare earth metals are used as a colouring agent in ceramic glazes. Cerium and yttrium are used for opacification of ceramic vessels. They are also used for making piezoelectric ceramics. In dental porcelain material, silver may be replaced by yttrium, samarium and lanthanum.
 3. **Incandescent lamp**: The intense white light emitted by the oxides of cerium and other rare earth metals on being heated, makes the mixed oxide suitable for use in cored carbon arc lamps for use in movie photography and projection, and in search lights for military purpose. Also, when dysprosium is added to the mercury or argon vapour in fluorescent light tubes, the output light becomes bright and intensified. Addition of 1-2% Ce-oxide to thoria enhances the whiteness and brightness of light.
 4. **Phosphor**: ‘*Phosphor*’ is the coating of fluorescent substance applied to surfaces for converting invisible ultraviolet rays to visible light. The fluorescence of some of the rare earth metals and compounds make them suitable as an additive to phosphors for various special uses. Yttrium and europium oxides are used in television screens. Europium-activated yttrium phosphor emits an intense red light and improves the colour reproduction of television picture tubes. Europium added to barium phosphate phosphor improves image quality of X-ray films. Different metals are also used in intensifying different colours in X-ray screen phosphors (e.g., europium – violet; gadolinium – yellow green; terbium – yellow green, violet and blue). Samarium is used as a phosphor coating on glass for absorbing infrared radiation.
 5. **Permanent magnet**: essential characteristics of all magnets are the minute circulating currents. These currents occur naturally in ferromagnetic materials. Permanent magnets depend solely on the persistency of these natural currents in contrast to the excited magnets (e.g., electromagnet) which depend on controllable energizing currents. The permanent magnets possess an intrinsic resistance to changes in magnetization over a wide range of field strength. For this purpose, three main conditions have to be satisfied. These are:

- (i) The particles must be smaller than the domain of influence of each circulating current, because otherwise, if a particle cuts across the boundary line between two domains, then the movement of two currents along that boundary line passing through the particle may result in gradual change in magnetization within the particle.
- (ii) Particles should show magnetic anisotropy i.e., their magnetic fields should be in one direction only, because multidirectional fields will tend to cancel each other.
- (iii) Particles should be aligned in a magnetic field, because otherwise, magnetic fields of all the particles will also be in randomly different directions and they will then tend to cancel each other.

Cerium, praseodymium and samarium alloyed with cobalt can be used in the construction of permanent magnets. These rare earth metals are suitable in this use, because

- (i) they possess intrinsic magnetic property
- (ii) they are amenable to powder metallurgical techniques by which extremely fine sized particles can be produced
- (iii) the fine powders are easy to fabricate in a manner so that they are aligned in the direction of their magnetic field.

Such permanent magnets fabricated by densely packing powders of the rare earth metal alloys are proving to be far superior in performance. Erbium also serves a good additive to permanent magnets. (see also chapters on nickel and cobalt).

6. **Laser:** '*Laser*' is the acronym of 'light amplification by stimulated emission of radiation'. An incident light excites the atoms within a laser substance which then emits back the radiation in an amplified state. If the atoms of the substance are already in an excited initial state, then the stimulation by the incident light adds to that excitement and amplification of emission may increase manifold. This initial excitement (or '*pumping*' as it is called) is provided by dispersing neodymium ions in a glass or a transparent crystal of yttrium-aluminium-garnet (YAG). This is the principle of use of rare earth metals in the construction of lasers. Europium, terbium and thulium are also suitable as pumping elements.
7. **Radar:** '*Radar*' is the acronym of 'radio detection and ranging'. It is essentially a sensor device. It operates by transmitting electromagnetic energy into the surrounding, and then detecting the energy reflected back by any object. If a narrow beam of this energy is transmitted by the detector antenna, then the direction from which the reflection comes and hence the bearing of the object, can be ascertained. In a radar device, a transmitter converts electrical power to electromagnetic energy in the desired wave length, which then go through a microwave amplifier. The ability of yttrium-iron-garnet to transmit short wave energy with low energy losses makes it suitable in this application. In microwave-controlling device, oxides of gadolinium, lanthanum and neodymium also find application.
8. **Artificial diamond:** Artificial stones are those combinations of elements that are not found in nature (in contrast to synthetic stones which are made by laboratory synthesis of the same elements as in natural ones like Al and O₂ to make ruby). Yttrium-aluminium-garnet (YAG) is used for making artificial diamonds. High refractive index (similar to that of diamond) and hardness of yttrium contribute to the suitability of YAG in this use.

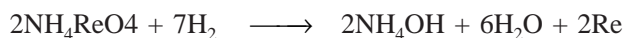
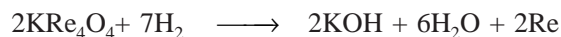
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- 9. Metallurgy:** The strong chemical affinity of the rare earths for various nonmetallic elements – particularly oxygen and sulphur, make them suitable for deoxidizing and desulphurizing metals (e.g., copper, titanium). For this purpose mischmetall is used. Also, the rare earths combine with the carbon of cast iron to form carbon nodules which increase the strength of the iron.
- 10. Alloys:** Rare earth metals can combine with various metals to form alloys. The common alloys are those of scandium with aluminium; of yttrium with iron, nickel and titanium; of lanthanum with iron and steel; of cerium with iron, steel, aluminium and magnesium; of praseodymium with aluminium and magnesium; and of neodymium with magnesium.
- 11. Atomic reactor:** Nuclear reactor houses the fuel elements, which contains a matrix supporting the nuclear fuel. Heat is generated within this fuel element due to chain emission of neutrons from the fissionable atoms of the nuclear fuel. Within a reactor, mechanisms are provided to regulate the generation of heat depending upon requirements. For regulating the heat, control rods called “moderators” that are capable of absorbing neutrons, are used. If the rods are lowered down in the reactor, more neutrons will be absorbed and the process of fission will slow down, thus reducing the heat. On the other hand, if the rods are pulled up out of the reactor, then less number of neutrons will be absorbed, and consequently the process of fission will accelerate, thus increasing the heat. Neutron-absorbing capacity makes gadolinium and europium suitable in such moderators. The same criterion makes gadolinium a suitable additive for neutron-absorbing paints.
- 12. Lighter flints:** The strong incandescence of cerium make it suitable for use in the form of Ce-Fe alloy making lighter flints such as those used in cigarette lighters, gas lighters etc. For this purpose, mischmetall can also be used.
- 13. Other uses:**
- (i) Synthetic garnet for computer memory (gadolinium, ytterbium)
 - (ii) Capacitors (lanthanum)
 - (iii) Semiconductors (yttrium, lanthanum)
 - (iv) Postage stamp glue (europium)
 - (v) Cracking catalyst in petroleum refining (oxides of neodymium, praseodymium, cerium and lanthanum)
 - (vi) Information storage for communication (gadolinium and lanthanum)
 - (vii) Plastic magnets of video tape recorders, head phones and cassette players.

RHENIUM

In 1925, two German chemists namely Ida Nodack and Walter Nodack discovered rhenium while, out of academic curiosity, looking for the missing elements of the Periodic Table predicted by D. Mendeleef. They obtained this metal by processing columbite. The name “rhenium” was coined by them after the river Rhine. Later on in 1928, it was obtained during treatment of waste liquors from molybdenite treatment plant, and later on from the potash smelter residues. Its average incidence in the earth’s crust is of the order of 1 ppb only.

RECOVERY

In 1942, it became more or less confirmed that molybdenite is the only economic source for rhenium recovery. Rhenium is present in MoS_2 in the form of sulphide, which, on roasting, is converted into oxide (Re_2O_7). This oxide being highly volatile, goes up the stack as white vapour along with flue dust and is trapped. The flue dust containing rhenium oxide is scrubbed, dissolved in water and is treated with KOH or NH_4OH to produce potassium perrhenate (KReO_4) or ammonium perrhenate (NH_4ReO_4) crystals. This is finally reduced with the help of hydrogen to yield rhenium metal powder according to the following reaction:



The rhenium metal powder is fabricated into rods, foils, strips etc. and marketed.

CRITERIA OF USE

Rhenium metal in powdered form is grey to brownish black in colour while in molten form it is silver white. But colour as such is not a useful criterion in its use. The useful criteria are as follows:

- (1) The electrically sintered rod made from molten rhenium is exceptionally hard.
- (2) It is a heavy metal; its specific gravity being 21.04.
- (3) It has a high melting point of $3180^\circ\text{C} \pm 20^\circ\text{C}$ next only to carbon and tungsten.
- (4) The rods made of rhenium are both ductile and forgeable.

- (5) It has relatively high electrical resistivity (4 times that of tungsten).
- (6) It is resistant to HCL acid, although not so to HNO_3 and hot H_2SO_4 acids which oxidize it.
- (7) It is inert at room temperature, and oxidizes to Re_2O_7 only at a somewhat high temperature of 400°C .
- (8) The oxide of rhenium is soluble in water and alcohol. The solution is acidic and can dissolve zinc and iron with evolution of hydrogen.
- (9) It alloys readily with tungsten, nickel, cobalt, tantalum, platinum, rhodium, iridium, gold, molybdenum and iron. These alloys have excellent corrosion resistance and other properties.

USES

Rhenium is seldom used alone. In most of the uses, it is alloyed with some other metal. Rhenium having high specific gravity is used in small objects or added in small quantities to other metals for imparting some desirable properties. Its common uses are as follows:

1. **Pen nibs:** Pen nibs are small objects, and so in this use, the weight is not very important, whereas the hardness and forgeability are. An alloy of rhenium (75%), rubidium (15%), niobium (7.5%) and beryllium (2.5%) is used. Rhenium imparts hardness, while at the same time it becomes relatively easy to forge the nib into the desired shape.
2. **Electric contact points & spark plugs:** The high melting point of rhenium makes it a useful alloying component.
3. **Thermocouples:** A thermocouple is used for measuring temperature, by virtue of the principle of thermo-electricity. If two dissimilar metals or alloys are soldered at their two end points, and one soldered junction is heated more in comparison to the other, then thermoelectric potential difference develops between the two junctions, and the voltage can be read on a voltmeter. By suitably calibrating the voltmeter in relation to the temperature difference, the temperature readings can be directly read. The high melting point of rhenium makes it a suitable metal for alloying with platinum, palladium, rhodium, iridium etc. for use in high temperature thermocouples.
4. **Bulb filament:** The high electrical resistivity, high melting point, hardness, ductility and inertness make rhenium a suitable material for use in filaments in light bulbs, radio bulbs, photoflash bulbs, mass spectrometers etc.
5. **Electroplating:** The corrosion resistance property of rhenium is harnessed in this application. It is used for electroplating thin coatings on surfaces of silver and brass.
6. **Superconductor:** Although rhenium is electrically resistant, due to the combination of its properties of hardness, ductility, inertness and alloyability, it has been used as an additive to some superconducting materials.
7. **Catalyst:** Rhenium heptasulphide, rhenium-copper alloy and colloidal rhenium have been used as a catalyst in hydrogenation of coal, ethylene, mineral oil etc. Rhenium heptasulphide is preferred to many other hydrogenation catalytic substances on account of its consistency and stability and insolubility in strong non-oxidizing acids.
8. **Jet propulsion engine:** Its resistance to extreme heat makes it an invaluable ingredient in superalloys used in the new generation jet propulsion engines.

RUBIDIUM

Rubidium, lithium, sodium, potassium and caesium constitute what is called the '*alkali group*' of metals. It was discovered in 1861 by R.Bunsel and G.Kirchnoff, and its name was derived from the Latin word 'rubidus' meaning dark red. The chief source of rubidium is lepidolite (lithium mica). It contains extremely low concentrations of Rb_2O (of the order of say 0.07%), and hence this metal is one of the costliest substances. It is recovered by decomposing lepidolite in sulphuric and hydrofluoric acids, to which then is added ammonium alum. Crystals of rubidium and caesium alums separate out. Rubidium is then recovered by fractional crystallization.

CRITERIA OF USE

Rubidium is highly reactive. It reacts readily with oxygen even at room temperatures. It has a silvery white colour. It has an isotope called Rb-87, which emits beta rays, has a half life of about 600 million years and decays to the stable end product strontium.

Rubidium has the property of photoemission, *i.e.*, it emits electrons when subjected to electromagnetic radiation such as light, X-rays etc. This property of photoemission is made use of in amplification of primary radiation energy, by suitably directing the photoelectrically liberated secondary electrons to impinge upon electrodes provided with a secondary emission coating. One of the most characteristic properties of rubidium is its ability to absorb light at a constant rate over a wide range of temperature.

USES

- (1) **Radio Vacuum tubes:** The property of photoemission has made rubidium useful material for amplification of radiation.
- (2) **Age determination of rock:** The ratio of Rb-87 content to strontium content in a rock and the knowledge of the half-life, can be the basis for determining age of rocks.
- (3) **Chemical compounds:** Due to its strong chemical reactivity, rubidium forms useful chemical compounds. For example, the iodide is useful in medicine. Various double salts and alloys of rubidium are also known. Some of the salts are used as micro-chemical reagents.

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- (4) **Hydrogenation:** Due to its strong affinity, rubidium reacts with water even at room temperature liberating hydrogen. Rubidium-mercury amalgam can be used as a catalytic agent in hydrogenation processes.
 - (5) **Mercury vapour lamps:** Photoemission capability is the criterion. (see the chapter on mercury).
 - (6) **Rubidium clock:** For measuring extremely small time spans – even up to quintillionth of a second (10^{-18} seconds) — accurately, atomic clock is used. Atomic clocks are of two types – cesium clock and rubidium clock. Rubidium clocks are portable and is now an integral component of '*Global Positioning System or GPS*'. These are also used for synchronizing the clocks of satellites with those of the network of base stations. Accuracy of rubidium clocks is 1 second in 1000 years. The ability of rubidium to absorb light at a constant rate over a wide range of temperature, is the key to its use in such clock, and the principle underlying its functioning consists in measuring this absorption. Vapour of Rb-87 is first sealed in a vial, and then is bombarded either by laser or by radiation from Ni-63 isotope. The rate of absorption of the light is measured and converted to the scale of time.

SILVER

Silver is one of the noble metals (the other two are gold and platinum). The average incidence of this metal in the earth's crust is less than 1 ppm. The principal minerals are argentite (Ag_2S), cerargyrite (AgCl), polybasite (Ag_9SbS_6), proustite (Ag_3AsS_3), and pyrargyrite (Ag_3SbS_3). But it commonly occurs in native state, and in association with gold, copper, lead and cobalt (sometimes). Primary silver production accounts for only about 17% of the world's total production and the rest 83% is recovered as byproduct. Of the total byproduct silver, about 37% is recovered from lead ore, 22% from copper ore and 13% from gold ore.

Silver from its primary ore is recovered by cyanide process or by flotation and smelting. However, the process for recovering byproduct silver depends on the principal ore. The silver in lead ore is recovered after smelting of the lead by what is called '*Parkes process*'. In this process molten lead is stirred with zinc and then cooled. The zinc crust containing silver separates out, and finally silver is recovered by distilling off zinc. From copper and gold ores, silver is recovered by electrolysis.

HISTORY

Silver is known since prehistoric times dating back to the 3rd millennium BC. During the 1st millennium BC, important centres of production developed in Greece and the activities continued there for several centuries with an estimated total output of 250 million ounces (about 7000 tonnes). In Roman empire also, silver was widely mined. Records of silver mining in Europe date back to the Middle ages while in USA it started in 1493. the mines of USA has long been exhausted. The total output from 1493 to 1953 has been estimated at 19700 million ounces (about 559000 tonnes). Till the 18th century, Bolivia topped the list of silver-producing countries. The now famous mines of Mexico commenced in 16th century, and from the beginning of 19th century Mexico became the top producer of this metal. In 1998, world's total production (both primary and byproduct) was 16000 tonnes (Primary: 4200 tonnes, byproduct :11800 tonnes) and in 2000, the production was 18390 tonnes. Mexico was the top producer followed by Peru, USA, Australia, China, Chile, Canada, Poland as the other important ones.

In India, it is recovered as a byproduct, but India's historical reputation was actually for the skills of the jewellers in mixing alloys, moulding, setting stones, inlay work, relief, drawing silver into fine wires, plating and gilding. The following table gives an idea of the production history of silver in India.

<i>Year</i>	<i>Approximate production</i>
1915	31 kg
1920	90 kg
1925	627 kg
1930	638 kg
1935	695 kg
1940	612 kg
1945	360 kg
1950	488 kg
1960	4.13 tonnes
1970	1.54 tonnes
1980	11.38 tonnes
April,1989-March,1990	34.98 tonnes
April,2000-March,2001	46.15 tonnes

CRITERIA OF USE

- 1. Colour and lustre:** Silver has a unique silver white colour, and it is capable of taking very fine polish.
- 2. Mechanical properties:** It is highly ductile and malleable. In fact, it is too soft for most use, and it is used in the form of some alloy. It has high strength and high fatigue resistance over a wide range of temperature.
- 3. Electrical and thermal conductivity:** Amongst the metals, it ranks first in conductivity of electricity and heat. Its electrical conductivity is 105 IACS i.e., 105% of that of copper.
- 4. Corrosion resistance:** It is strongly resistant to corrosion, oxidation and organic acids (hence nontoxic). It is practically indestructible.
- 5. Alloyability:** It can form alloys with a number of metals like copper.
- 6. Fusibility and solubility:** Silver fuses at 1050°C and dissolves in nitric acid.
- 7. Superstition and tradition:** Like gold, silver was also originally sought and treasured by ancient man out of fear which gave way to superstition and finally to tradition. In the Stone Age, people sported ornaments made of teeth and bones out of belief that they will ward off evil spirits and cool down nature's anger. Silver ornaments were used for much the same reason. That superstition became so much ingrained in the minds of people down the generations, that even now on certain special occasions in some countries like India, people – particularly women – buy silver irrespective of whether they need or not. Rational thinking may not justify such purchases, but the forces of history and tradition are too strong to shun the habit.

- 8. International price:** Silver as such being indestructible, jewellery ware and other ornamental objects made of it is never consumed, and silver in these forms remains as its overground reserve. Nobody knows for certain how much silver is in stock in these forms. It has been estimated that till 2005, the total silver reserve held overground all over the world is 40 billion ounces (about 1134 million tonnes) out of which the quantity held in Indian homes as jewellery and utensils is 4 billion ounces (about 113 million tonnes). The demand of silver, therefore, to a large extent, can be met through circulation of the already held silver, and not necessarily through fresh production from mines. In fact about 35% of this stock gets circulated every year. The international price of silver is determined mainly by this overground reserves, and this price influences its demand and usage to a large extent.

USES

Of the total world consumption of silver, about 70% is used in four industrial applications (electrical, electroplating, medical and photography), and only 30% in other applications including fabrication of jewellery. The important uses are as follows:

- 1. Jewellery:** It is one of the earliest uses of metallic silver. The relative rarity of occurrence, resistance to corrosion, indestructibility, ability to take very fine polish, unique colour and easy workability on account of ductility and malleability – all together play the key role in this use.
- 2. Silver ware:** Ability to take a high degree of polish, resistance to organic acids present in food stuff, and easy workability into various desired shapes on account of malleability are the principal criteria in this use.
- 3. Coinage:** Earlier, in many countries like India, UK, silver and silver-based alloys were popular materials for coin-making. In 1941, brass coins with 1% nickel added to brass (alloy of copper and zinc) were introduced. But since 1946, nickel-copper alloy has become a standard coin replacing silver coins. The high malleability makes it easy to work into flat-shaped coins. Also durability due to resistance to corrosion, and other criteria like rarity (hence natural high value), attractive colour and bright lasting shine were the main criteria for its use as coins.
- 4. Electrical application:** Though silver is the best electrical conductor amongst all metals, its use in power transmission is ruled out because of high costs. Its use as electrical conductor is limited to very heavy duty and high-tech machines and instruments like television, computers etc. and those required in military operations and scientific research. In such applications, a very high degree of efficiency is a must while, at the same time, only small quantities of silver are required. It can be used in the form of thin wires and in the form of alloys (with copper, zinc etc.) as silver solders for making electrical connections. Its ductility, ability to retain strength over a wide range of temperatures and ability to form alloys are the key criteria, besides the exceptionally high electrical conductivity.

5. **Heavy duty equipment:** The high strength and fatigue resistance of silver over a wide range of temperatures coupled with malleability makes this metal suitable for making bearing plates of military aircrafts and other heavy duty critical machines.
6. **Electroplating:** The unique silver white colour, bright lustrous finish and resistance to oxidation and organic acids make silver desirable in electroplating of utensils, decorative articles, ornaments etc.
7. **Photography:** Silver is used in the form of silver bromide for making black and white photographic films. This chemical is light-sensitive. On being struck by a ray of light, it is activated and can be reduced to metallic silver by a film developer solution. Silver bromide which is not thus activated, cannot be reduced by the developer. It is applied as an emulsion containing 40% silver bromide crystals, 50% gelatin as binder and 10% water. In complete darkness, the silver bromide emulsifies in gelatin solution, and is then applied on a thin dark coloured anti-halo layer coated on the surface of a thin base made of cellulose nitrate or cellulose acetate or metal to make a photographic film or plate. The size of the silver bromide crystals determines the light sensitivity (or speed) of the film. Coarser the crystals, higher will be the speed. Silver bromide is not sensitive to all colours, and so, for making coloured films it has to be sensitized by adding ions of gold, mercury etc.
8. **Medical surgery:** The high degree of ductility and strength facilitate making of suture wires used in surgery. Malleability renders it possible to make thin plates for use in surgery. Some silver compound can be used for dental filling. The resistance to the organic acids of human body renders silver and its compounds desirable in these applications.
9. **Zari:** This is also called “*metallic Zari*”. Zari is a specially made thread used for fine embroidery by skilled artisans of India (specially Surat). There is a mention of this art in Prehistoric times of *Rig Veda* as dresses of gods and goddesses. However, this art flourished due to patronization of the Mughal kings of India during the Medieval times. In real Zari, silver wires are wrapped with gold paper, drawn and then wound around silk threads. In imitation Zari, copper wires are coated with silver (or sometimes with gold) by either electroplating or chemical process, are wound around ordinary yarn, and then thinned to make fine threads of Zari. Ductility and strength of silver are the key criteria.
10. **Alloys:**

“Ashtadhatu” or alloy of eight metals	Au, Ag, Cu, Pb, Sn, Fe, bronze and brass	This was first made during the prehistoric era, by mixing all the metals and their alloys that were known and available then. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship.
Sterling silver	7.5% Cu; balance Ag	Copper imparts the necessary hardness to silver so as to facilitate its fabrication into jewellery and other usable products.

11. **Varakh:** '*Varakh*' is an edible thin cover put on top of sweets in India to make it attractive-looking and presentable. Varakh is an ultra-thin silver foil less than one micron thin. This is made by repeatedly pounding a strip of pure silver. The attractive silver–white colour, malleability, nontoxicity and softness of pure silver are the key criteria.
12. **Superconductor:** Laboratory scale experiments in the National Physical laboratory, India in the 1990s on high-temperature silver-sheathed bismuth oxide based superconductor were encouraging.
13. **Silver battery:** These batteries have a zinc anode and silver chloride cathode. The electrolyte consists of an aqueous solution of lithium chloride or zinc chloride and zinc sulphate.
14. **Wound healing:** Ancient Greeks knew the healing power of silver when applied to wounds. Now, this ancient knowledge and the nascent nanotechnology have been combined in a bandage coated with nano-sized silver particles. When this bandage is applied on a burn, the silver particles penetrate into the skin and fight the nano-sized bacteria and viruses more efficiently so as to effect expeditious healing.

SODIUM

Sodium metal was isolated by Sir Humphrey Davy who was the first to isolate it in 1807. It is recovered by electrolysis of molten sodium chloride (NaCl). Since the melting point of pure NaCl is high — 800°C, calcium chloride (CaCl₂) is added to the bath to depress the melting point to about 580°C.

Sodium metal is a hazardous substance inasmuch as (i) the moment it comes in contact with hydrogen, hydrogen ignites and explodes, and even in contact with water, the metal catches fire (ii) if in contact with body, the flesh burns, (iii) it causes acute irritation to eyes. This requires extreme care in its handling such as covering with dry nitrogen and storing in air tight, rust-free metal vessels out of contact with water.

CRITERIA OF USE

Sodium is a lighter-than-water metal having specific gravity 0.97 at zero temperature, which decreases further with increase in temperature. But the most important criteria for its practical use are its low melting point, low boiling point, good thermal conductivity, alloyability with potassium and lead, and chemical reactivity.

It melts at 97.5°C. It boils at 883°C under atmospheric pressure, but under low pressure conditions, the boiling and vaporization take place at much lower temperatures. The hot vapour glows with yellow light in absence of oxygen, and burns in yellow coloured fire in presence of oxygen.

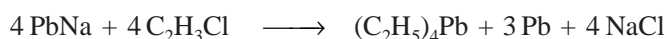
Thermal conductivity of solid sodium at about 21°C is 0.32 cal/sec/cm²/°C, but it increases with increasing temperature, and that of liquid sodium at 200°C is considerably high – 0.93 cal/sec/cm²/°C (cf. the figure for copper is 0.941).

The metal has strong chemical affinity for chlorine and other halogens, hydrogen etc.

USES

Many sodium-based industrial products are actually made from sodium chloride. So far as sodium metal is concerned, its uses are limited mainly due to its hazardous nature. For most uses, the commercial grade metal of 99.8% purity is enough, but for use in nuclear reactor, still purer special grade is required. The important uses are as follows:

- 1. Tetra-ethyl lead:** This chemical reduces the knock of the mo-gas (petrol) in internal combustion engines such as those used in cars. Octane number is a measure of ‘anti-knock’ value of a motor fuel i.e. the ability to resist the knock or sound produced due to its sudden and violent combustion in a spark ignition engine. For this measurement, a standard scale has been devised by assigning the value zero to heptane (C_7H_{16}) which has very poor knock resistance, and 100 to octane (C_8H_{18}) having a very high knock resistance. Octane number is the percentage of this isomer of octane in its mixture with heptane. Tetra-ethyl lead [$(C_2H_5)_4Pb$] is a good and inexpensive anti-knocking agent. It is synthesized by reacting the alloy Pb-Na (90%Pb, 10%Na) with ethyl chloride [C_2H_5Cl]:



The lead metal produced can be recycled.

This chemical was the largest industrial use of sodium in the past. But now-a-days, due to the high content of lead in the exhaust gases of the cars posing threat to human health by lead poisoning, it is being phased out in most countries including India in preference to “lead-free petrol” either containing other additives like benzene or by modifications in the refining technology.

- 2. Coolant in nuclear reactor:** For transferring heat generated within fuel elements in a nuclear reactor, coolants are used. One of the coolant materials is liquid sodium metal. The low melting point of sodium means that the temperature of this liquid metal is considerably lower than the heat generated within the reactor. Good thermal conductivity of sodium — particularly in liquid form — are also a deciding criterion. But for this purpose, the containers are required to be made of some special material (*e.g.*, beryllium) with which sodium does not react. But even then, most metals are prone to be attacked by oxygen, if any present, at the high temperatures involved. So, the sodium should ideally be totally free from oxygen. However, in reality, some traces of oxygen is present in sodium. Calcium metal is therefore incorporated in the system. Calcium preferentially reacts with the oxygen and forms a stable oxide.

Instead of sodium, the alloy Na-K is also used for this purpose, the advantage being that this alloy remains partly liquid even at room temperature.

- 3. Sodium vapour lamp:** The nature of sodium vapour to glow, when heated, with a yellow light is the main criterion besides relatively low temperature at which it vaporizes under conditions of low pressure. A sodium vapour lamp consists of a heat-resistant almost vacuum glass tube containing two electrodes, sodium and the inert neon gas. The pressure within the tube is extremely low – 0.004 mm of mercury. Electric current is passed through the electrodes raising the temperature to $280^\circ C$. Under these pressure-temperature conditions, the sodium vaporizes and glows with a bright yellow light. It takes some time for the temperature to rise sufficiently and for sodium to vaporize, and that is why these

lamps start glowing after a few minutes from switching on. They are, therefore, not suited to home use where frequent switching on and off is involved, but to conditions where, once switched on, are not required to be switched off before a long time (*e.g.*, street lights).

- 4. Other uses:** In the past, sodium found application in reduction of animal and vegetable fats to alcohol, but now hydrogenation is the preferred process.

The strong chemical affinity of sodium with hydrogen and halogens is taken advantage of in making sodium hydride and in reducing uranium and zirconium halides respectively. Besides, certain chemical compounds like sodium amide, sodium cyanide and sodium peroxide are made from the metal.

TANTALUM

Tantalum was discovered in 1902 by a Swedish chemist named Ekebeg. He named it after the Greek god Tantalus, because he had a tantalizing time trying to dissolve it in acid. The commercial ore is tantalite, which is a member of continuous iron-manganese isomorphous series having the general formula $[(\text{FeMn})(\text{NbTa})_2\text{O}_5]$, occurring in pegmatite and in placer sand derived from it—often associated with cassiterite. If tantalum is more than niobium, then the mineral is called tantalite, if niobium is more, columbite. But both these metals occur together, and there is no exclusive ore of tantalum alone. Tantalite and columbite are both valued for extraction of both the metals. Commercial grade tantalite should contain a maximum of 40% Ta_2O_5 and a minimum of 60% ($\text{Ta}_2\text{O}_5 + \text{Nb}_2\text{O}_5$).

As much as 65% of world's tantalum supply come as byproduct from the tin slag of the Afro-Asian countries. So far as India is concerned, some occurrences were recorded during the period 1855- 1943, mainly in pegmatites; and during 1943-44, at least 820 kg of tantalum ore was reported to be produced and exported to USA. Prompted by a spurt in world demand and consequently, in cost during the last few decades, serious exploration to find recoverable tantalum in the cassiterite-bearing sands of India was started in 1974 by the Atomic Energy Commission. There is, however, no report of production of this metal in India till 2005.

RECOVERY

Tantalite is generally obtained as a byproduct of cassiterite sand mining, and also during mining of pegmatite for minerals like mica, beryl, cassiterite etc. The tantalite is fused with caustic soda to get a mixture containing iron, manganese and sodium-niobium tantalate. The mixture is digested in concentrated hydrochloric acid. Solid tantaloniobic acid precipitates, while the iron and manganese remain in solution, are filtered out and discarded. The tantaloniobic acid crystals are dissolved in hydrofluoric acid followed by addition of potassium fluoride to obtain a solution containing tantalum-potassium fluoride and niobium-potassium oxyfluoride. On cooling, the former precipitates and recovered by filtration as residue, while the latter going with the filtrate is subjected to further processing to extract niobium. The tantalum-potassium fluoride is fused and then electrolyzed to obtain pure tantalum metal, tantalum is marketed in the form of wire, ingot, powder or strip.

CRITERIA OF USE

Tantalum is a very heavy silvery white highly refractory metal having specific gravity 16.6. Its heaviness is not only an enabling factor in its concentration from the cassiterite-bearing sands, but also in some industrial applications. The other main properties for which it is valued by the user industries, are:

- (1) It is soft, malleable and remarkably ductile, while at the same time very tough with high mechanical strength.
- (2) Tantalum is a refractory metal. Its melting point is high at 2996°C, and that of its carbide is also very high – about 4000°C.
- (3) It is resistant to corrosion and inert to attack by most acids – even at temperatures up to 150°C; only fused alkalis, hydrofluoric acid and a mixture of nitric and hydrochloric acids can slowly dissolve it.
- (4) It absorbs gases when heated.
- (5) It does not irritate human tissues.
- (6) It is a good electrical conductor (13.9% of copper *i.e.*, International Annealed Copper or IACS).
- (7) Its electrical properties remain stable over a wide range of temperatures starting from (–) 55°C to (+) 125°C. This is a unique attribute.
- (8) It can form alloys with carbon and certain metals.
- (9) Its oxide has high refractory index.

USES

The following uses of tantalum are significant from the industrial point of view.

- (1) **Large high vacuum valves:** Such valves are used for radio broadcasting and reception. The role of tantalum here is as an absorbent of gases.
- (2) **Chemical equipment and pipe-lining:** High mechanical strength combined with extremely high resistance to chemical attack make tantalum a valuable material for constructing chemical equipment and in lining for steel and copper pipes.
- (3) **Orthopedic materials:** Tantalum is used in making of cranial plates for treating skull injuries, and pins, wires, screws and suture wire for orthopedic operations. The most important criteria are its high mechanical strength, non-irritancy to human tissues, malleability, ductility and easy workability.
- (4) **Cutting tools and dies:** Tantalum carbide is one of the hardest substances known and it is used in tools for cutting very hard metals and alloys. Hardness and high melting point makes it suitable for making high temperature dies in combination with tungsten carbide. Such dies are used for fine wire drawing.
- (5) **Hardening agent:** High mechanical strength and corrosion resistance make tantalum suitable for hardening spinnerets, fountain pen nibs, and surgical and dental instruments.
- (6) **Rectifier:** A rectifier is a device which allows an electric current to flow in one direction but not in the opposite direction. It consists of an anode and a cathode filament heated by current. From the heated cathode, freed electrons flow towards the anode, and thus a conductive connection from the cathode to the anode is established –either directly in a

vacuum or through ionization of an inert gas medium. But the anode is made of a substance that will not be heated enough to emit electrons, and consequently, current will not flow from it towards the cathode. This, in essence, is the principle of a rectifier. Rectifiers are used for converting alternating current to direct current as required in battery-chargers and in battery eliminators for radio sets. Tantalum is a refractory metal and a good conductor of electricity too. So, when serving as an anode in a rectifier, the heat generated by the impact of the electrons from the cathode is not enough to cause its own electrons to be released and emitted back towards the cathode. Thus, current flows only in one direction, *i.e.*, from the cathode to the anode. Also, the atmosphere of vacuum or inert gas prevents it from oxidation.

- (7) **Capacitors and other electronic equipments:** Tantalum has recently generated considerable interest because of its use in capacitors in electronic equipments. Capacitors perform a vital function, storing electricity for a short period of time and ensuring that the current supplied remains within a narrow range of parameters – particularly in low voltage applications like mobile phones, in which the tolerance range is very tight. The advantage of using tantalum lies not only in its good electrical conductivity stable over a wide range of temperature (-55°C to 125°C), but also in its high specific gravity that enables miniaturization of the capacitors into low-volume high-performance equipments. This unique combination of advantages is not matched by other capacitor materials like ceramics.

Tantalum being a good electrical conductor, is also used as anode and grid material for transmitting tubes in electronics.

- (8) **Alloys:** Tantalum has a very limited use in steel alloying. However, it is used in some industrial alloys with nickel, chromium, tungsten, magnesium, calcium and niobium.
- (9) **Aircraft industry:** There is a trend to use metals like tantalum in jet propulsion engines, because of its high refractoriness. Such engines get good thrust from fuel and perform better.
- (10) **Other uses:** The high refractive index of tantalum oxide make it a suitable additive to glass for making special highly refractive glass (*e.g.*, camera lens). Tantalum oxide is used as an additive to glasses for aircraft lenses. High ductility, high strength, high melting point and good electrical conductivity of the metal enable it to be drawn into a very fine, strong, refractory and electrically conductive wire for evaporating other metals by passing high voltage current. Its high melting point combined with strength makes it usable for cementing tungsten carbide powder for making tools. Porous tantalum compacts and tantalum foils are used in electrolytic condensers. Tantalum-potassium fluoride was used as a catalyst in synthetic rubber manufacturing during World War-II.

THALLIUM

Thallium was discovered by W. Crookes in 1861 during spectroscopic study of some rocks. It produces spectral band of typical green colour resembling that of a budding twig. Thallium owes its name to the Greek word 'thallos' meaning budding twig. However, its potentiality for practical use was recognized in 1896. It is never found in nature in free state, and traces of it occur associated with some zinc ores and pyrites. Its incidence in the earth's crust has been estimated to vary from 1-3 ppm.

RECOVERY

Thallium is recovered from the flue dusts of zinc smelters. The flue dust is first treated with sulphuric acid whereby thallium sulphate is produced. But the acid also converts the cadmium that may be present in the ore, into its sulphate. So, actually a mixture of thallium and cadmium sulphates is usually obtained at this stage which, when subjected to electrolysis, yields a cadmium-thallium alloy. This alloy is treated with hot water and sodium carbonate to produce carbonates of cadmium and thallium. The former precipitates while the latter, being soluble, can be filtered out. This separated thallium carbonate is converted back to thallium sulphate by first treating with hydrogen sulphide and then with sulphuric acid. Thallous sulphate is a commercial product by itself. Metallic thallium in the form of sponge can also be recovered from it by electrolysis.

CRITERIA OF USE

Thallium does not appear to possess any particularly remarkable property, and moreover, its high cost and limited availability act as deterrents against its wide spread use. However, thallium does find some industrial use due to the following properties.

1. **Specific gravity:** Specific gravity of the metal is high – 11.85 at 20°C. It is slightly heavier than lead (specific gravity 11.34).
2. **Thermal properties:** Melting point of thallium is relatively low – 302.5°C. It is even lower than that of lead (327°C). A peculiar property is that although its freezing point is many times higher than that of mercury (– 39°C), its addition to mercury as an alloying metal results in substantial lowering of the freezing point of the latter.
3. **Mechanical properties:** It is so soft that it can be cut by a knife and scratched by a nail. It is highly malleable.

- 4. Chemical properties and alloyability:** Thallium has strong chemical affinity for elements like sulphur, phosphorus, halogens, oxygen etc. Some of the compounds are poisonous. It is easily alloyable with a number of metals.
- 5. Optical properties:** Although the metal is white, its oxides are coloured. For example, thallos oxide (Tl_2O) is yellow while thallic oxide (Tl_2O_3) is violet to dark brown. Certain other compounds also possess some useful properties like ability to transmit infrared rays, and sensitivity to low intensity light and other kinds of electromagnetic radiation.

USES

Thallium is used mostly as a chemical compound and an alloy as additives, and only in a few uses in its metallic form. The important uses are as follows:

- 1. Rodenticide and fungicide:** Both the sulphate and the carbonate of thallium are poisonous. But while the former is insoluble in water, the latter is soluble. The sulphate is used as a rodenticide, because rodenticides are usually mixed with food for killing rodents, insects etc., and solubility is not a criterion. The carbonate is used as a fungicide, because fungicides are to be sprayed, and so, should be soluble in water. Thallium sulphate or thallium carbonate may also be used for coating textile, rubber, leather etc. to protect them against insects and fungi.
- 2. Infrared signaling device and infrared spectroscopy:** In this application, the compound thallium bromoiodide, which is in the form of crystals and which is capable of transmitting infrared, is used. This has particular utility in military operations for sending signals through invisible infrared light. Similarly in infrared absorption research, spectrometers fitted with special lenses and optical plates containing this compound are used.
- 3. Photoelectric cell:** When light-sensitive metal is exposed to the energy of light radiation, electrons may be liberated from the atoms. If, after liberation, the electrons remain within the metal, then the phenomenon is called '*photoconductive effect*'; and if the electrons are ejected, then the phenomenon is called '*photoelectric effect*'. In a photoelectric cell, there is a light-sensitive cathode from which electrons, so ejected, flow through an evacuated or inert gas-filled tube into an anode. If the circuit is completed, then electric current will flow. This principle is applied to camera exposuremeters, solar batteries etc. Certain substances are so sensitive to light that their electric resistance drops sharply on increasing the light intensity, and consequently those substances can be very useful as the cathode in photoelectric cells. Thallium oxysulphide is one such substance. The electric resistance drops by as much as 50% upon exposure to only 0.25 foot-candle of light.
- 4. Gamma radiation scintillation counter:** In this, the photo-multiplication effect produced due to secondary emission of electrons, is employed. In a photo-multiplier, when high energy electromagnetic radiation (light rays, X-rays, gamma rays etc.) strikes on a substance, electrons may be ejected. Certain substances emit several secondary electrons for each primary electron striking it, thus producing a multiplication effect. Thallium-activated sodium iodide crystals can serve this purpose in scintillation counters for detection of gamma radiation.
- 5. Low temperature thermometer:** Addition of 8.5% thallium to mercury produces an alloy with freezing point ($-$) $60^{\circ}C$ (cf., freezing point of mercury alone is ($-$) $39^{\circ}C$ and that of thallium alone is $302.5^{\circ}C$). This alloy is suitable for measuring temperatures in the range of ($-$) $60^{\circ}C$ to ($+$) $20^{\circ}C$.

6. **Alloys:** Thallium is added in suitable quantities for adjusting certain properties – particularly malleability and softness/hardness. For example, due to its addition, malleability of antimony, bismuth, gold and platinum decreases while that of copper, lead and zinc increases. It may be added in small quantities to solders (alloy of lead and tin) for making them a bit softer.
7. **Glass:** Thallium is added to glass either as such or in oxide form with a view to imparting some special properties as follows:
 - (i) Special low-melting glasses for applying to electronic devices as protective coatings against humidity and oxidation, can be made by adding a little thallium which has a lower melting point than glass and which is colourless.
 - (ii) Due to its high specific gravity, thallium may be added for making dense glass and synthetic gems. Higher density of such glasses and synthetic gems also serves to increase their refractive indices.
 - (iii) Oxides of thallium may be added for imparting various colours (yellow to dark brown) to glass.

SUBSTITUTION

For most of the uses of thallium, alternative materials exist, and as such it is not indispensable. In USA, its use as rodenticide has been banned since 1965, and it is substituted by organic chemicals which are harmless to human health.

TIN

Tin is a scarce metal with incidence in the earth's crust 2 ppm (49th amongst all elements). Only one mineral namely, cassiterite (SnO_2), theoretically containing 78.6% tin, is mined and processed. The name comes from Cassiterides Islands, off the western coast of Europe from where there is evidence of ancient tin mining. It is also known as *tin-stone* and *tin-ore*. In nature, however, the cassiterite is found mixed with mainly SiO_2 and oxides of iron. The other minerals of minor commercial importance are Stannite [$\text{Cu}_2\text{S}(\text{FeS})\text{SnS}_2$], Teallite [PbSnS_2], Cylindrite [$\text{PbSn}_4\text{FeSb}_2\text{S}_{14}$], franckeite [$\text{Pb}_5\text{FeSn}_3\text{Sb}_2\text{S}_{14}$], which are not mined as such, but as minerals associated with the cassiterite. Cassiterite is mined from stream placer as well as from vein.

HISTORY

Tin is an ancient metal, its use being supposed to be known during the prehistoric period. The metal culture is believed to date back to 4000 BC when the *Copper Age* began, as deciphered from evidences found in Turkey. This was followed by the *Bronze Age* which marked the advent of tin in human life in the form of bronze (an alloy of copper and tin). The early Greeks, the Phoenicians, the Persians and the Chinese were not only familiar with the usage of bronze for weapons, implements, utensils, ornaments, coins etc., but developed new tin-bearing alloys like solder (lead and tin), pewter (lead, tin and antimony) etc. The Romans, it is believed, valued copper and tin so much that they fought wars and expanded their empire into Spain, Portugal, England and Cornwall – the counties rich in natural resources of these metals in those days. By the beginning of the Christian Era, the art of tin-plating or *tinning* copper was known and practised. But tin-plating of iron – a major technologic basis for use of tin today – had to wait till 16th century. As per available records, Cornwall was the principal producer of cassiterite and tin since 500 BC. Malaya, which was the second most important cassiterite-producing as well as tin-smelting country earlier, and China, the principal tin-producing country of today, also has a history of centuries of tin production. Other countries and regions namely, Indonesia, and continental Europe were also significant contributors. Cassiterite used to be mined from streams till at least the beginning of Christian Era, and vein mining was developed later. It has been estimated that the total world production of tin metal till 1800 AD was about 4 million tonnes.

Tin industry, however, recorded substantial growth quite late, i.e., during the later half of 19th century much after the Industrial Revolution had begun. Australia joined the band of tin-producing

countries around 1950, Bolivia in 1860, and Congo and Nigeria mainly after 1910. USA has all along been deficient in tin ore resource, and the growth of tin-smelting industry here has also been a post World War-II (1940-1945) phenomenon. The world tin production between 1800 AD and 1950 AD has been estimated to be over 10 million tonnes. The world production of tin metal increased at a slow pace from 183000 tonnes in 1953 to 242000 tonnes in 2001.

In India, there is no evidence of any organized tin cassiterite mining either in the ancient or in the modern times. Sporadic small scale mining operations were recorded intermittently in some small pockets of cassiterite-bearing rock between the years 1849 and 1915 in a village called Purgo near Parasnath hill in present Jharkhand state. In all, 4 to 5 attempts – none exceeding a couple of years – were made. But apart from those, there has neither been any discovery of tin ore deposit nor any mining till 1978. Since that year, unorganized mining involving digging and panning of cassiterite-bearing stream sand by local villagers in Govindpal-Tongpal area of Bastar district in Chhattisgarh state, and smelting in plants located in Raipur and Jagdalpur in the same state have been going on. Later on, a couple of smelting plants based on imported concentrates have been set up in Mumbai and Cuttack district. The production of metal increased from a mere 18 kg in 1978 to 6.75 tonnes in 1980 and then to 18.11 tonnes and 22.20 tonnes in 1985 and 1990 respectively. Production history of tin metal since that year is as follows:

<i>Year</i>	<i>Production</i>
1978	18 kg
1980	6.75 tonnes
1985	18.11 tonnes
1990	22.20 tonnes
April 1992-March 1993	62.77 tonnes
April 1995-March 1996	19.02 tonnes

For recent years, production statistics of metallic tin have not been published, but that of tin concentrate was 13.89 tonnes and 10.63 tonnes during 2001-02 and 2002-03 (April-March periods) respectively.

RECOVERY

Extraction of tin from its ore involves a series of processes as follows:

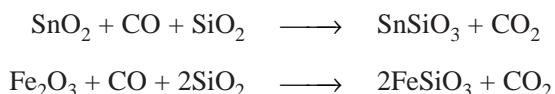
- 1. Concentration:** Cassiterite-bearing placer sand is easier to concentrate than lodes. In case of the former, the sand is washed with the help of bucket-line dredges or by hydraulic method involving directing a jet of water, to wash out the lighter waste minerals. The heavy minerals including cassiterite grains are recovered with the help of screens and sluice boxes. The concentrate thus recovered, is subjected to further cleaning by hand methods to eliminate most of the heavy minerals other than cassiterite. The final concentrate containing even 75% Sn (cf., 78.6% Sn in pure cassiterite) is not uncommon.

In case of the cassiterite lodes, concentration involves grinding and ore dressing based on the high specific gravity of cassiterite (6.8-7.1) compared to that of most of the associated minerals. But the recovery is low and the process is cost-intensive.

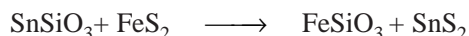
2. Metallurgy: Pure cassiterite or very high grade concentrate recovered from placer sand can be easily reduced to tin metal by heating with charcoal, CO, hydrogen gases etc. at low heat in either blast furnaces or (more commonly) reverberatory furnaces. But, since the concentrates usually contain some SiO_2 and iron oxides, tin tends to form silicate, stannates and Fe-Sn alloy resulting in losses of tin metal. Besides, very small amounts of arsenic, copper, lead, tungsten, antimony, bismuth and sulphur may also be present. Depending on the impurities, the concentrate is subjected to the metallurgical processes involving either the roasting-smelting-refining route or the chemical method.

(a) Roasting-smelting-refining:

- (i) *Roasting:* It is desirable if sulphur, antimony, arsenic and tungsten are present in excess amounts as impurities. During roasting, a considerable part of these elements are driven off as oxides or as vapours. Elimination of substantial parts of these impurities will reduce the cost of their removal during the post-smelting refining. If tungsten is high, then the concentrate is sintered with soda ash to form sodium tungstate, which may be leached out.
- (ii) *Smelting:* Depending on the nature of impurities, the concentrate is subjected to smelting either directly or after roasting. The purpose of smelting is to extract an impure product of tin metal. With the impurities SiO_2 and iron oxides, tin tends to form silicate. In principle smelting involves heating either the concentrate or the product of roasting to $1100\text{--}1300^\circ\text{C}$ with coal or charcoal. The reactions are:



The fused ferrous and stannous silicates form the liquid slag and some un-reacted carbon may also be present. The surplus SnO_2 gets reduced to metallic tin, and the liquid tin, being heavier, settles at the bottom of the furnace, and is trapped and cooled as “*block tin*”. At this stage, some amount of pyrite (FeS_2) is added to the fused slag. The reaction that follows, can be indicated thus:



The SnS_2 volatilizes at the furnace temperature and the vapour is captured, oxidized to SnO_2 , and finally reduced to metallic tin with the help of some reductant like coal, charcoal HC-gas.

- (iii) *Refining:* The tin obtained after smelting may still contain a little iron, copper, lead, arsenic, antimony and bismuth depending on their presence in the concentrate. For removing these impurities the tin is refined for which there are two processes – drossing or fire-refining and electro-refining.

In fire-refining, the impure tin is melted in a hearth and maintained at a temperature slightly above the melting point of tin but below that of iron-tin alloy. Some tin forms the alloy and settles at the bottom of the hearth as a semisolid to solid mass. The molten tin containing the other impurities is then stirred with a green pole. The stirring exposes the impurities and the tin to air. The impurities and a part of the tin are oxidized forming a hard film on the surface called *dross*, while the pure molten tin metal is allowed to settle below it. The melt of pure tin metal is ladled out. Some tin is, of course, lost in the tin-iron alloy and in the tin oxide.

In electro-refining, the electrolyte used is a mixture of H_2SiF_6 and H_2SO_4 acid to provide sulphate radical. Arsenic, antimony, bismuth, copper and all the other impurities except lead are deposited on the anode, while tin and lead, being close in position in the electromotive series, move towards the cathode. The lead combines with the sulphate radical of the electrolyte to precipitate as lead sulphate (thus being prevented from depositing along with tin), and tin alone is deposited on the cathode.

(b) Chemical method:

A chemical method called “*Cavaet process*” has been developed to treat tin ore directly without the need of concentration. This process involves chloridization, volatilization and electrolysis. The ore is ground to 8-mesh size, dried and roasted in a rotary kiln at 800°C with charcoal and calcium chloride. Cassiterite after being reduced by carbon, combines with chlorine to form stannous chloride. The deleterious elements like antimony, arsenic and copper also form chlorides. All these chlorides are volatile. While the stannous chloride vapour easily dissolves in water, the other chlorides are precipitated. The solution containing stannous chloride is taken out by filtration, and is electrolyzed. The tin metal deposited on the cathodes, is removed and cast into ingots.

CRITERIA OF USE

There are two allotropic forms of tin namely, “*alpha tin*” (100% pure tin) and “*beta tin*” (99.8% pure tin containing 0.2% of Pb, Sb, Ag, Bi). The beta tin is the natural metal in crystalline form, a bar of which, when bent, gives off a cracking sound due to friction amongst the crystals, and this sound is called “*cry of tin*”. After years of exposure to ($-$) 13°C , it changes to the amorphous alpha form with graying of colour, decomposition to powder, about 20.85% decrease in specific gravity and roughening of surface. The roughness is often referred to as “*tin disease*” or “*tin pest*”. By tin normally the beta or natural tin is understood, and it is this tin that is used in various ways. Uses of tin depend on a number of its unique physical and chemical properties. These are as follows:

A. Physical properties

- (a) *Thermal*: Tin has a low melting temperature compared to most metals. Its melting point is 231.9°C , and it boils at $2265\text{-}2270^\circ\text{C}$. Thus it has a long liquid phase, but in between, at about $1100\text{-}1200^\circ\text{C}$, it starts vapourizing. The liquid tin, on solidification, practically does not shrink, the shrinkage being up to only 2.8 per cent.
- (b) *Specific gravity*: Tin is heavy. The specific gravity of solid metal is 7.29 and that of liquid metal at melting point is 6.97.
- (c) *Colour and lustre*: It is white in colour with bright metallic lustre.
- (d) *Workability*: Tin is soft, pliable and ductile at 100°C . Hence, it can be worked at low temperature by rolling into extrusions, and drawn and spun into wires. But if small amounts of SnO_2 is dispersed in it, then it becomes hard.
- (e) *Wetting power*: Liquid tin adheres to clean iron, steel, copper and copper alloys, lead and many other substances but not to glass.
- (f) *Alloying ability*: Tin readily forms alloys with a number of metals like copper, nickel, gold, silver etc., which are soluble in liquid tin.

- (g) *Friction*: Tin has a very low coefficient of friction (co-efficient of friction is the ratio of the friction force to the applied force).
- (h) *Electrical conductivity*: Pure tin metal is a good conductor of electricity having conductivity 16.6% that of copper (International Annealed Copper Standard or ICAI).

B. Chemical properties

- (a) *Reactivity with acids and bases*: Tin is amphoteric, i.e., it reacts with both strong acids and strong bases.
- (b) *Corrosion resistance*: It is resistant to nearly neutral or weak solutions of acids or bases.
- (c) *Toxicity*: Tin is non-toxicant to human system.
- (d) *Ability to form chemical compounds*: Tin forms a number of inorganic and organic compounds by reacting with oxygen, sulphur, chlorine etc., which in turn find many uses.

Some of these criteria like the thermal properties, the specific gravity and the ability to form chemical compounds are made use of in extraction of tin from its ore.

USES

Tin is mostly used in the form of alloys and compounds, but a few applications are based on pure tin also (but not cent percent pure alpha tin which tends to decompose on exposure to cold environment). The uses are:

- (1) Tinning or tin-plating (containers, IC engine pistons)
- (2) Roofing sheets
- (3) Solder
- (4) Dental amalgam
- (5) Alloys (bronze, gun metal, babbitt metal, bearing metal etc.)
- (6) Wine bottle caps
- (7) Tin foils (collapsible tubes)
- (8) Float glass manufacturing
- (9) Fuse wire
- (10) Chemical compounds (special glass, textile, additives, poultry medicines, catalyst etc.)
- (11) Tin powder
- (12) Tin shot

The details of these uses are as follows:

- (1) **Tin-plating**: This is probably the second oldest use of tin after bronze. There is historical evidence of use of tin-plated vessels before 23 AD. Cans commonly referred to as “tin cans” are actually tin-plated iron cans. Tin hardly accounts for 1.5% of the weight of an empty beverage can (that too the high specific gravity of tin notwithstanding), and the thickness of tin is of the order of 0.3 microns. White colour, bright lustre, low melting temperature, high wetting power, good workability, resistance to weak acids and bases (as in case of food stuff), corrosion resistance and in-toxicity are the main criteria for use of tin-plated food-containers and beverage cans in preference to ones made of iron alone. Iron slowly dissolves and affects the flavour and appearance of the food or the beverage, and tin serves as an effective protective cover. Good workability facilitates easy forging of the cans and containers into any desired shape.

In IC engine, tin-plated aluminium pistons are preferable mainly because of the low coefficient of friction of tin and also the other properties like good workability, low melting temperature, high wetting power and corrosion resistance. Tinned brass, tinned copper wire and tinned lead pipes are also manufactured.

There are three processes for tin-plating/tinning/tin-coating namely, hot-dip process, electrolytic process and spraying.

- (a) *Hot-dip process*: In this process, the base-sheets are passed manually or automatically through a tin pot containing molten commercial tin, flux and palm oil maintained at a temperature of around 327°C, washed and cooled. The tin pot is made of iron sheet with brick lining. The role of palm oil is to provide hydrocarbon reductant and together with the flux, it serves to remove the impurities that may be present in the commercial tin.
 - (b) *Electrolytic process*: In this process, tin-plating is achieved by precipitation of tin in an anodizing bath through electrolysis. The bath consists of a compound of tin (fluoride, chloride, fluoroborate, sulphate etc) dissolved in either an acid (acid bath) or an alkali (alkali bath). The surface to be plated serves as the cathode. Electric current flows from the anode bath towards the cathode surface and the bath is electrolyzed releasing tin ions which are deposited as a very thin film of tin metal on the plated surface. The acid used may be phenosulphonic acid. In the alkali bath, alkaline stannate is used as the electrolyte.
 - (c) *Spraying*: Liquid tin may be sprayed on metal for making tin-coated equipment, decorative objects etc.
- (2) **Roofing sheet**: In this product of tin, iron sheets plated with tin containing some lead is used. For this, what is called “*terne-plating*” of iron sheets is carried out. The term “*terne*” is a French word meaning dull. The addition of lead makes the tin dull. The technology of *terne-plating* is similar to that of tin-plating. The positions of tin and lead in the electromotive series are close to each other, and their ions move together towards the iron surface (cathode) to be plated. This closeness is made use of in *terne-plating*.
- (3) **Solder**: Solder is an alloy of tin and lead, which is used for joining two pieces of a metal by a process of welding called “*soldering*”. It is sometimes called “*soft solder*” to distinguish it from “*silver soldering*” which is hard and which contains neither tin nor lead. Early Romans used two types of solders – very soft *Tertiarium* containing lead and tin in 2:1 ratio, and somewhat harder *argentarium* containing lead and tin in 1:1 ratio. The latter type is commonly used now-a-days. In solder the role of lead is to soften it, and that of tin is to lower the fusion temperature as well as to strengthen the bond by virtue of its adhering power. However, soldering is not a suitable welding process for very high temperature applications requiring a very high strength of the bond. But, on the other hand, it is the most suitable process where (i) high temperature may melt and damage the parts to be joined, and (ii) precision – more than strength – is required. Electronic parts of television, computer etc. may be cited as examples.
- (4) **Dentistry**: Powder containing 60% silver, 27% tin and 13% copper mixed into a paste with mercury is used for filling dental cavities. Here, the main role of tin is to increase the adherence of the material to the wall of the cavity. Also, its white colour, softness, non-toxicity, and resistance to corrosion by weak acids and alkalis of the food stuff and the digestive secretions, add to the advantages.

- (5) **Alloys:** Tin can form alloys with a number of metals, to improve their performances in various applications by virtue of its physical and chemical properties. The following is a list of the common alloys containing tin as one of the constituents.

<i>Alloy</i>	<i>Composition</i>	<i>Functions/Uses</i>
Brass	75% Cu; 21% Zn; 3% Pb; 1% Sn	Suitable for valves, pressure tight castings, plumbers' fittings, ornamental castings.
Naval brass	62% Cu; 36.75% Zn; 1.25% Sn	Good resistance to corrosion in salt water. Used in the form of sheets and extrusions.
Gunmetal or admiralty bronze	88% Cu; 10% Sn; 2% Zn	Corrosion resistant in marine conditions. Used in general utility construction parts.
Phosphor bronze	87.75–89.5% Cu; 10–12% Sn; 0.25–0.5% P	Low coefficient of friction. Suitable for use in bearings of wheels including worn ones, which are under heavy load.
Porous bronze	87% Cu; 10% Sn; 3% graphite	Sintered product. Can be soaked in oil before use. Used in small motors not accessible to regular lubrication, such as those of domestic appliances, starters of automobiles, business machines etc.
Leaded bronze	76% Cu; 9% Sn; 15% Pb; 2% Ni	Acid resistant bronze for use in poor lubricating conditions. Used in bearings of cranes and earth-moving equipment.
Bell metal or speculum or beta-bronze or high-tin bronze	20-30% Sn; balance copper	High tin content makes the alloy brittle with poor ductility and hence not suited to engineering applications; used for casting into consumer articles like mirror, kitchen ware, idols, bells etc.
Tin-based white metal or Babbitt metal	88.25% (min) Sn; 3–4% Cu; 7–8% Sb; 0.5% Pb	Low coefficient of friction. Used in bearings of automobiles and in engineering works.
Pewter	Pb and Sn with addition of Sb	Antimony has a hardening effect. Old use dating back to Roman Era. Used in domestic and church decorative metal ware. Pewter is an old English term for anything rich in tin.

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<i>Alloy</i>	<i>Composition</i>	<i>Functions/Uses</i>
Low aluminium-tin	5.5–7.0% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium's machinability with improved strength; used in bearings where very high anti-friction properties are not essential.
High aluminium-tin	20–40% Sn with small additions of Cu, Ni, Si and Ce	Combines properties of white metal and aluminium's machinability with improved strength; used in bearings where very high anti-friction properties are essential.
Leaded aluminium alloys	8% Pb; 1% Cd; 1–4% Sn	Cheaper alternative to Al-Sn, Cu-Pb, Sn-Pb alloys. Used in passenger car bearings.
Titanium aluminium tin alloy	Ti 91–94%; Al 4–6%; Sn 2–3%	Used in aircraft tailpipe assemblies, sheet components subjected to up to 500°C temperature, gas turbine compressor rings, missile fuel tanks.
Titanium aluminium molybdenum tin silicon alloy	Ti 87.5%; Al, Mo and Sn each 4%; Si 0.5%.	High strength alloy, used for highly stressed structural components in aircraft and structural engineering.
Fusible tin alloy	Sn, Bi, Cd, In	Low melting point. Suitable for die-casting. Also used in boiler safety plugs, seals, fire extinguishers, fire alarms.
“Ashtadhatu” or alloy of eight metals	Au, Ag, Cu, Pb, Sn, Fe, bronze and brass	This was first made during the prehistoric era, by mixing all the metals and their alloys that were known and available then. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship.
“Panchadhatu” or alloy of five metals	Alloy of Sn, Cu, Pb, Fe and brass	This is one of several types of “Panchadhatu” first made during the prehistoric era. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship. It is a cheaper version of “Ashtadhatu” sans gold and silver.

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<i>Alloy</i>	<i>Composition</i>	<i>Functions/Uses</i>
Ternary copper-nickel-tin spinodal alloy	Cu 85%; Ni 9%; Sn 6% or Cu 77%; Ni 15%; Sn 8%	“Spinode” is a Greek word meaning cusp. This alloy is made by controlled thermal treatment called spinodal decomposition resulting in uniform dispersions of tin-rich phases in the copper matrix, and is characterized by high mechanical strength, high wear resistance and high corrosion resistance in sea water and acid environments. Used in high-productivity mould tooling for the plastic industry; high-performance bearings for aerospace and heavy duty mobile industrial equipment; and highly corrosion resistant components for undersea oil and gas exploration.

- (6) **Wine bottle caps:** Softness, attractive appearance, non-toxicity and resistance to corrosion by weak acids or alkalis are the main criteria. Softness allows it to be opened easily and safely.
- (7) **Tin foils:** Softness and workability enable this metal to be cold-rolled into thin foils. Foils of pure tin are used for wrapping cheese, chocolates, tobacco, electrical condensers, cables, gun charges, and for making collapsible tubes by extrusion. Tin tubes were originally used for making artists’ colour tube around the middle of the 19th century. Being costly, such tubes are now not ordinarily used (like aluminium tubes for tooth paste), but for special applications meant for food paste and mustard paste (e.g., for consumption of astronauts in space ships), pharmaceuticals, cosmetics, adhesives, paint products etc. Non-toxicity and resistance to corrosion by weak acids or alkalis are the main criteria for preserving the food and keeping it hygienic. These properties were recognized even in the prehistoric era, and Egyptian mummies have been found wrapped in tin foil.
- (8) **Float glass manufacturing:** The concept of float glass is comparatively new to India, having entered here in 1990s. Float glass is a type of sheet glass that is exceptionally smooth on both surfaces and free from internal stress. For its manufacturing, molten glass at 1100^o C is discharged from the furnace onto a bed of molten tin, where it floats and spreads out freely in the form of a long strip. It is, then cooled either slowly (annealed float glass) or suddenly (heat-strengthened float glass). Low melting point, very low shrinkage on solidification, higher than glass specific gravity, non-adherence to glass surface, and low coefficient of friction (allowing the molten glass to spread freely without any resistance) are the key properties of tin in this application.
- (9) **Fuse wire:** Pure tin can be used for making very thin (0.2 mm diameter) fuse wires due to its high ductility and electrical conductivity. Being easily fusible at low temperature, such wires melt and break immediately whenever there is an extra current. These are useful to protect very sensitive electronic parts.
- (10) **Chemical compounds:** Tin has ability to form inorganic compounds with chlorine, oxygen, sulphur, potassium and indium, and also organic compounds called “*organotin compounds*”. The compounds and their uses are:

- (i) Stannous chloride (SnCl_2): Catalyst in olive oil refining, and a weighting agent for silk.
 - (ii) Stannous sulphate [$\text{Sn}(\text{SO}_4)_2$]: Used in electronics.
 - (iii) Potassium stannate: Used in electronics.
 - (iv) Zinc stannate and zinc hydroxy stannate: Flame and smoke inhibitor, fire retardant.
 - (v) Indium tin oxide: Computer display panel.
 - (vi) Stannic oxide (SnO_2): Good conductor of electricity, optically transparent and high-strength. Used for making special glasses as 1 micron thick films on low-intensity lighting panels, display panels, fluorescent lights and cathode ray tubes (good electrical conductivity) and as less than 0.1 micron thick films on aircraft windshields (strength and optical transparency). Also used to opacify enamel.
 - (vii) Organotin compounds: These are organic compounds of tin with carbon, and made from stannic chloride. These compounds find use as additives to PVC (as a stabilizer), transformer oil (to prevent slow decomposition by formation of acid), chlorinated rubber paint (to prevent release of HCl under action of sunlight), and as medicine for curing intestinal worms in chickens and turkeys. A compound namely, tin oleate is used in lubricating and textile oils.
- (11) **Tin powder:** Tin powder is used for making decorative paper and solder paste, and for metal spraying. The powder is produced by the technique of *atomization* (atomization is the process of dispersion of a molten metal into small particles by a rapidly moving stream of gas or liquid).
- (12) **Tin shot:** Since the beginning of the 21st century, the industry researchers have been experimenting with non-toxicant tin shot to replace lead shot in hunting and gun sports to protect the food chain from lead poisoning.

WASTE UTILIZATION

Tin is a recyclable metal. Secondary tin is mainly reclaimed from used tin plates and the process is known as “*detinning*”. Next to tin plates, tin scrap generated during fabrication of primary tin metal, account for the production of secondary tin. Tin waste and scrap are traded internationally in significant volumes.

The process of detinning essentially consists of treating the tin plate clippings in a caustic soda solution. Tin reacts with caustic soda to form a liquor of sodium stannate along with the metallic impurities present in the tin plate. Then this liquor is electrolyzed by which tin is deposited on the cathode and is removed. Before electrolysis, however, lead, whose position in the electromotive series is almost the same as that of tin and which moves towards the cathode together with tin, is removed.

SUBSTITUTION

Because of the unique combination of properties, there is no direct and perfect substitute of tin. The only point that goes against tin is its high cost. For this reason, various cheaper and practical alternatives have come up. Tetra packs, enamel steel and steel coated with an organic substance have come in a big way to replace tin beverage cans. Glass, plastic and paper are used for day-to-day packing of food and household necessities. Aluminium and its foil have substituted tin in utensils and wrapping respectively. Galvanized iron and asbestos sheets have largely replaced tin in roofing sheets.

TUNGSTEN

The name tungsten is derived from the Swedish words “tung” meaning heavy, and “sten” meaning stone. It is not found in native state. Its principal ores are wolframite [(Fe, Mn)WO₄] and scheelite [CaWO₄]. Wolframite actually represents the intermediate stage in the series ferberite [FeWO₄] – huebnerite [MnWO₄]. Theoretically, wolframite i.e., the iron-manganese tungstate contains an average of 76.5% WO₃ (tungsten trioxide) or 51% W, and Scheelite i.e., the calcium tungstate contains an average of 80.6% WO₃ or 64.1% W. But in nature, the tenor of tungsten deposits is usually less than 1 per cent. Wolframite is a heavy mineral with specific gravity between 7.0 and 7.5 and also magnetic. It commonly occurs in pegmatite and granite veins, and in placer sands, often associated with cassiterite. Scheelite is also heavy having specific gravity of around 6. Other minerals of tungsten are not of any economic significance.

HISTORY

Tungsten was first identified and isolated during 1781–83 from wolframite by two Swedish chemists J. Jose and F. de Ethuyar. Record of its first use dates back to 1847. Its first use for manufacturing of alloy steel was patented in 1855, but the product was marketed for the first time in 1898. With the invention of electric bulb in the early part of the 20th century, use of tungsten got a fillip. Thereafter, its other uses were developed. But its utility in heat-resistant high-speed iron alloys and in very hard carbide, made it a strategic metal and ups and downs in its production were linked with wars, starting from the World War-I in (1914–18) to the World War-II in (1940–45), Korean War (1953) and so on. In the early period of its history, Myanmar (erstwhile Burma), dominated the world production and supply. Later on China, Korea, USA, Portugal, Bolivia etc. became important producers. The average annual world production of the concentrate (60% WO₃) was recorded as over 3500 tonnes (mainly from Myanmar) during the period 1914–18, followed by a slump; then it revived to about 34550 tonnes in 1939 and 56900 tonnes in 1943 only to decrease again to about 18000 tonnes in 1947, but it revived in 1948 to 27000 tonnes. It stood at the level of 58000 tonnes in 2001.

India was never a significant contributor of tungsten to the world production. Its production here has been small, sporadic and intermittent. The most noteworthy deposit namely, Degana in Rajasthan, was first reported by O.M. Heron of Geological Survey of India in 1913, and its mining began that year in a small way. Later on, it was worked seriously – but only during the periods of World War-I

(1914–18) and World War-II (1940–44). Its production (in terms of concentrate) was about 146 tonnes in 1913, and during the period 1937–46, the average annual production was a mere 36 tonnes. The production history from 1950 onwards was:

<i>Year</i>	<i>Production</i>
1950	3 tonnes
1953	15 tonnes
1954	600 kg
1960	3 tonnes
1965	13.7 tonnes
1970	34.9 tonnes
1975	37.6 tonnes
1980	44.1 tonnes
1985	51.3 tonnes
1990	22.6 tonnes
April 1995-March1996	6.5 tonnes

The mines gradually closed down after 1995 due to dwindling resources, high production costs and decrease in price.

RECOVERY

Tungsten is recovered and marketed in three forms namely:

- (1) scheelite concentrate/ synthetic scheelite
- (2) ferrotungsten
- (3) tungsten metal powder

These intermediate products are actually used for the different end-products based on tungsten.

(1) Scheelite concentrate/synthetic scheelite: The standard marketable grade of these products is 60% WO_3 . The high specific gravity of the ores of tungsten make them amenable to concentration by gravity methods. The ore is crushed and ground, and then concentrated, generally, by jigging and tabling. Sometimes, flotation technology is also employed. The grade of the natural ore may be improved to 50–70% WO_3 or even more. While high grade concentrates obtained from scheelite are normally suitable for direct charging for processing to various intermediate or final products, those from wolframite are not suitable because of its manganese content, and hence these are converted to what is called “*synthetic scheelite*” having the same composition as natural scheelite i.e., $CaWO_4$. This synthetic scheelite, like the high grade natural scheelite concentrate, is suitable for direct charging.

The low-grade scheelite concentrates and the wolframite concentrates are subjected to ore dressing, leaching, roasting, magnetic separation, and sintering and digestion – for removing certain deleterious constituents and for production of synthetic scheelite. Ore dressing helps removal of cassiterite; leaching with hydrochloric acid is for removing phosphorus; roasting for driving off

sulphur (as SO_2), antimony, bismuth and arsenic; magnetic separation for separating scheelite from wolframite; sintering and digestion for production of synthetic scheelite. In the latter process, the wolframite and the low grade scheelite concentrates are sintered with sodium carbonate, dissolved under pressure in caustic soda as sodium tungstate, and then CaCl_2 is added to the solution to precipitate CaWO_4 , while the manganese and iron of wolframite remain in solution. For certain uses molybdenum, lead, zinc and copper are undesirable, and it may be necessary to remove them, if present. This is done by filtering out their sulphides, which do not go into solution and precipitate, before addition of CaCl_2 .

(2) Ferro-tungsten: This contains 70-80% W (ideally 78%). This is generally used as a vehicle for adding tungsten to steel for manufacture of all types of tungsten-bearing alloys, but it is, though superior, costly to manufacture. A low grade version of it called “*melting base*” containing only 35% W is sometimes used for making low-tungsten alloys. Besides tungsten, the maximum limits of various elements in industrial grade ferro-tungsten are specified as: *Mn 0.75%; C 0.6%; P and S each 0.06%; Si 1.0%; Cu, As and Sn each 0.1%; Sb 0.08%; and Mo 0.6% (if the intended alloy product is high-tungsten low-molybdenum steel).*

The manufacturing technology, in essence, consists of reduction of scheelite in an electric arc furnace with the help of a reductant – either carbon or silicon. It can also be made by aluminothermic and silicothermic processes. Some acid slag (silica) or basic slag (calcium silicate) is also added to the furnace to maintain a reasonably high volume of slag in order to remove maximum possible amounts of sulphur and phosphorus (vide the chapter Iron Ore –Hematite, Specifications of pig iron).

(3) Tungsten metal powder: Tungsten metal is produced from scheelite concentrates. For this purpose, hydrochloric acid is added to the concentrate to obtain tungstic acid crystals, which are washed and dissolved in ammonium hydroxide. The resultant ammonium tungstate solution, on heating, yields ammonium paratungstate crystals, which are reduced by either carbon (lampblack, natural gas etc.) or hydrogen to produce metallic tungsten in the form of powder. The carbon-reduced product contains some carbon as impurity, while the hydrogen-reduced one is free from this impurity.

CRITERIA OF USE

Tungsten has a greyish white colour, but the industrial use of the metal is based mainly on:

- (1) **Density:** Tungsten is a heavy metal with specific gravity of 17.
- (2) **Strength and ductility:** Tungsten has the highest tensile strength amongst all metals – even at high temperature. But at the same time it is ductile.
- (3) **Melting point:** It has the highest melting temperature amongst all metals — 3382°C .
- (4) **Thermal expansion:** Its thermal expansion is low – $4.43 \text{ ppm}/^\circ\text{C}$, and is similar to that of boro-silicate glass.
- (5) **Hardness:** Amongst all the metals, it has the highest recorded hardness.
- (6) **Alloyability:** It has abilities to form alloys with a number of ferrous and nonferrous metals.
- (7) **Chemical:** It forms chemical compounds with carbon, iodine etc.

- (8) **Corrosion resistance:** It is highly resistant to corrosion by oxidation and by acids.
- (9) **Electrical conductivity:** It is a good conductor of electricity (31% of standard copper i.e., International Annealed Copper Standard or IACS).

USES

Scheelite concentrate, ferrotungsten and tungsten metal powder are used for manufacturing various end-products. The important ones are:

- (1) Alloys
- (2) Tungsten carbide tools
- (3) Tungsten carbide shells
- (4) Tungsten carbide jewellery
- (5) Electric bulb filament wire
- (6) Heavy-duty electrical contact points
- (7) Shielding of radioactive material
- (8) Rectifier
- (9) X-ray tube
- (10) Welding rods
- (11) Sealing
- (12) Tungsten chemicals

These end-uses are discussed as follows:

- (1) **Alloys:** Both natural/synthetic scheelite and ferrotungsten are used as the feeds. The former can be used as a direct feed for production of a particular type of tungsten-bearing alloy of steel that contains less than 6.75% W and a relatively high percentage of molybdenum. However, the scheelite concentrate for this purpose must be of a very high grade. The main criterion is the cost factor. Scheelite is used for making those types of low-tungsten alloy where additional costs on account of further processing of scheelite can be avoided. On the other hand ferrotungsten is used for making other types of alloys containing 6.75% or more of tungsten. When added to iron and steel, it combines with a part of the carbon present in pig iron or steel to form tungsten carbide that makes steel hard and strong at elevated temperatures. The important tungsten-bearing alloys of steel along with their uses are:

<i>Alloy</i>	<i>Composition</i>	<i>Uses</i>
(i) 9% tungsten hot die steel	0.3% C; 2.5% Cr; 9.0% W	Hot forging and punching dies for rivets; bolts; extrusion pads; die-casting dies for aluminium and copper alloys.
(ii) Silicon-chromium-tungsten shock resistant steel	0.55% C; 1.0% Cr; 2.0% W; 0.6% Si	Chisels; snap and caulking tools; heading and nail dies; engrossing punches.

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<i>Alloy</i>	<i>Composition</i>	<i>Uses</i>
(iii) 18% tungsten general purpose high speed cutting steel	0.75% C; 4.5% Cr; 18.0% W; 1.25% V	Drills; reamers; lathe tools; broaches; milling cutters; punches; dies.
(iv) 12% cobalt super high speed steel	0.8% C; 4.5% Cr; 21.0% W; 1.25% V; 12.0% Co	Heavy duty machining on high tensile alloy steel; forged products; close-grained cast iron products; railway coach tires.
(v) Stellite	25–30% Cr; 1% (max) Mo; 2–15% W; 0.25–3.3% C; 3% (max) Ni; 2% (max) Si; 1% (max) Mn; balance Co	Used in hard facing materials (e.g., armaments, cutting tools).
(vi) Tungsten-bearing super-alloys	W and Cu or Ag	Used in chemical industry, resistance welding, heavy duty electric contacts, turbine blades.

- (2) **Tungsten carbide tools:** Tungsten carbide (WC) is an alloy of tungsten and carbon. It is produced by mixing the metal powder with lampblack and heating the mixture. Tungsten carbide tools are produced by sintering (i.e., insipient fusion) a mixture of tungsten carbide and cobalt or nickel in dies of desired shapes. Such tools are highly wear-resistant (due to hardness and strength) and resistant to softening at high temperature (due to high melting point of tungsten). Hence they are suitable for use under high temperature operating conditions, as in drilling bits. Hardness and high melting point makes tungsten carbide suitable for making high temperature dies in combination with tantalum carbide. Such dies are wear-resistant at high temperatures, and are used for fine wire drawing.

In the late 1980s, the US Bureau of Mines developed a microwave induced plasma (MIP) process for producing very fine WC powder very quickly.

- (3) **Tungsten carbide shells:** Heaviness of tungsten, in addition to strength and high melting point, make tungsten carbide for use as a core in high velocity armour-piercing shells and darts.
- (4) **Tungsten carbide jewellery:** In this application, the hardness, ability to retain lustre for long time and hypo-allergenic nature (no allergic reaction) of the carbide are taken advantage of.
- (5) **Electric bulb filament wire:** This is an important application of tungsten metal powder. An ordinary electric bulb consists of a filament made of an electrical conductor, through which current is passed raising the temperature of the conductor and causing it to glow and emit light. Earlier, carbon conductors were used, but they could not be heated to very high temperature and so the light used to be dim. Now, the preferred substance is tungsten metal.

For making a tungsten filament, tungsten powder is first compressed to a rod shape, and sintered at 1000°C in an inert gas atmosphere (to prevent oxidation) by passing electric current. The rod is about 3 mm in diameter. It is then wire-drawn in cold state through

diamond drawing dies (holes). The wire is of 0.01 mm (10 microns) diameter. The wire in the form of a coil is welded to thicker support wires and encased in a glass bulb, the inside of which is either vacuum or filled with some inert gas to prevent oxidation during glowing. The current, when entering the thin filament from the thicker support wire, meets with high resistance due to reduction in the cross sectional area and as a result, it glows and emits light. The intensity of heat and light is directly proportional to the length of the filament in the coil. Tungsten is an electrical conductor, and its fusion temperature is very high, making it suitable for this use.

In halogen bulbs, tungsten iodide filament is used instead of tungsten metal. The iodide can withstand much higher intensity of heat, and give out brighter light. However, the iodide vapour tends to corrode the glass, and hence, the filament is encased in an inner quartz bulb within the glass bulb. The ability of tungsten to form iodide comes as an advantage in this application.

Addition of 0.8-1.2% of thorium inhibits crystal growth, controls grain size and increases ductility thus prolonging the life of tungsten filaments.

- (6) **Heavy duty electrical contacts:** Distributor point, horn, speed governor and spark plug tips of automobiles are examples of such contacts. High electrical conductivity and low arc erosion due to high melting point are the main criteria. Tungsten metal powder is used.
- (7) **Shielding of radioactive material:** Tungsten is used for this purpose in nuclear reactors. The main function of a reactor is primarily (i) to contain the dangerous radioactive emissions, and (ii) to prevent loss of the heat generated within it. Normally, the reactor walls consist of thick shields of steel and concrete. But tungsten sheets along with steel are more effective, because tungsten adds to the strength, density and refractoriness of the walls. For manufacturing tungsten sheets, the tungsten metal powder is compressed, sintered by passing electric current, swaged into flat plates, and then cold-rolled into sheets.
- (8) **Rectifier:** A rectifier is a device which allows an electric current to flow in one direction but not in the opposite direction. It consists of an anode and a cathode filament heated by current. From the heated cathode, freed electrons flow towards the anode, and thus a conductive connection from the cathode to the anode is established –either directly in a vacuum or through ionization of an inert gas medium. But the anode is made of a substance that will not be heated enough to emit electrons, and consequently, current will not flow from it towards the cathode. This, in essence, is the principle of a rectifier. Rectifiers are used for converting alternating current to direct current as required in battery-chargers and in battery eliminators for radio sets.

Tungsten is a refractory metal and a good conductor of electricity too. So, when serving as an anode in a rectifier, the heat generated by the impact of the electrons from the cathode is not enough to cause its own electrons to be released and emitted back towards the cathode. Thus, current flows only in one direction, i.e., from the cathode to the anode. Also, the atmosphere of vacuum or inert gas prevents it from oxidation.

- (9) **X-ray tube:** X-rays (or Roentgen rays) are short wave electromagnetic vibrations which can penetrate solid matter. When a stream of very fast high-energy electrons released from a cathode, strikes a metallic anode, it suddenly slows down, and the electrons penetrate into the metal. Inside the metal, a high-energy electron strikes a host atom and displaces an electron of that atom, creating a vacancy. The vacancy is then filled up by another electron

of the host from another orbit. As a result of these disturbances in the equilibrium of the host atoms, radiation in the form of X-rays is emitted.

The role of tungsten in an X-ray tube is to release the electrons from the cathode, for which a white hot incandescent tungsten filament fed with high-voltage direct current from a transformer through a rectifier.

- (10) **Welding rod:** Tungsten metal powder is used as a coating for hard-facing of welding rods. Strength, high melting point and electrical conductivity of tungsten are the main criteria.
- (11) **Sealing:** Similar thermal expansion of tungsten vis-à-vis boro-silicate glass makes it a suitable material for glass to metal seal.
- (12) **Tungsten chemicals:** This is a minor use of tungsten. Cadmium tungstate has been used in preparing X-ray screens; sodium tungstate as a fire-proofing agent for cloth; and calcium or magnesium tungstate in the inner surfaces of fluorescent tubes. Some tungsten chemicals are also used in pigments, dyes and inks. Tungstic oxide or WO_3 is one such compound which is a bronze yellow coloured pigment, and because of its colour, it is called "*tungsten bronze*". The sulphide *i.e.*, WS_2 is stable at temperatures up to $500^\circ C$, and is used in high temperature lubricants.

SPECIFICATIONS OF USE

The basic raw material for production of other intermediate products (ferrotungsten, tungsten carbide and tungsten metal powder) as well as for direct charging to steel, are synthetic scheelite and natural scheelite concentrate. The former is made from wolframite and the latter from scheelite – the two types of ore mined. Of these two types of raw materials, synthetic scheelite is a chemically processed high grade product, the impurities associated with the wolframite having been taken care of in the different steps of processing. It is the other type of raw material namely, natural scheelite concentrate, that contains certain deleterious constituents carried forward from the scheelite ore. The user industries which consume scheelite concentrate, therefore, specify the limits of various constituents for different uses. These are as follows:

- (1) **Tungsten-based steel alloys:** The market value of concentrate is for its contained tungsten which in turn is expressed in terms of WO_3 . In the scheelite concentrate meant for direct charging to steel, the minimum content of WO_3 is generally specified to be 70 per cent. The preferred maximum limits of other constituents are: *Sn, S, As, Pb and Zn each 0.1%; Cu and P each 0.05%; Mn and S each 0.5%; Bi 0.25%; Mo 0.8% (if the intended alloy product is high-tungsten low-molybdenum steel); slime content nil.*

The very purpose of alloying tungsten with steel is for increasing hardness, strength and melting point of the latter. It is apparent that presence of any element which is less hard, less strong and less refractory than tungsten will defeat that very purpose. For this reason the metals Sn, Cu, Pb, Zn, Sb, As, Bi and Mn are undesirable in the concentrate. Mn is not supposed to be present in scheelite ore, but it may get into the concentrate from some admixed wolframite. The melting temperature of molybdenum ($2620^\circ C$) is comparable with that of tungsten, its hardening effect on steel is 2-3 times more powerful than tungsten. Hence, although its presence in a little amount in the tungsten alloy may be beneficial, too much will tend to make the steel too hard for most uses.

If phosphorus is carried into the final product i.e., steel, it reduces ductility and makes the steel brittle under shocks. Likewise sulphur, when carried to the final product i.e., steel, produces cracks at the edges at the time of rolling of the steel. Both these elements are extremely difficult as well as costly to remove beyond a certain point. Hence these impurities are highly objectionable.

Slime is extremely fine grained and creates handling problems. Hence, users prefer nodulized concentrate.

- (2) **Ferrotungsten:** The manufacturing involves high temperatures and use of acid or basic slag, the quantities of which are within the control of the producers. This enables them to remove most of the impurities. Hence, the tolerance limits of the deleterious constituents in the concentrate meant for this product, are more flexible than in case of the concentrate meant for direct charging to steel.
- (3) **Tungsten carbide:** The minimum WO_3 -content in the concentrate meant for this product should be 65%, although the industries prefer 70 per cent. The maximum limits of other impurities should be: *Sn, Cu, Sb, As, Mo, Pb and Zn each 0.1%; P 0.05%; S 0.5%; Bi 0.25 per cent.* the reasons for their undesirability are the same as in case of alloys. The grain size of the carbide, which depends on that of the original powder used for its manufacture, is very important. Since the tungsten carbide tools are made by sintering an aggregate of its grains, too fine a grain size will make the process difficult to control, and too coarse a size will not make the tool homogeneous and strong. However there is no standard specification.
- (4) **Tungsten powder filament:** The maximum limits of the objectionable constituents in the concentrates generally preferred by the industries are: *Mo 0.002–0.025%; Sb 0.005–0.05%; As 0.02% and P 0.05 per cent.* Molybdenum reduces the strength and infusibility of the filaments. Also, the process of powder production involves precipitation of tungstic acid and ammonium paratungstate crystals at different stages. Arsenic and phosphorus lead to formation of ultra-fine colloidal precipitates which interfere with the precipitation of crystalline grains of the tungsten compounds, leading to difficulty in the subsequent reduction process.

VANADIUM

In 1601 a Mexican scientist called Del Rio discovered what he thought was a new metal and named it 'erythronium'. But other scientists, told him that he had merely rediscovered chromium and the matter was not pursued further. In 1830, when a Swedish chemist named Nils Sefstrom discovered a new metal, he named it vanadium after the Norwegian goddess Vanadis. Since then the credit of discovering vanadium has been attributed to Sefstrom, although, later on, Vohler established that Sefstrom's vanadium and Del Rio's erythronium were actually the same. The main sources of vanadium in the world are patronite [vanadium sulphide; VS_4] and carnotite [hydrated vanadate of uranium and potassium: $K_2O \cdot 3U_2O_3 \cdot V_2O_5 \cdot 3H_2O$]. Other important ores are roscoelite [vanadium mica; $2K_2O \cdot 2Al_2O_3 \cdot (MgFe)O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O$] and vanadinite [$Pb_4(PbCl)(VO_4)_3$]. Besides, bravoite [$(FeNiV)S_2$], sulvanite ($3Cu_2S \cdot V_2S_5$), vanadiferous magnetite, ashes of certain coals and lignites, asphalt and certain sandstones and bauxites also contain significant amounts of vanadium. Its crustal incidence is however rather low, being 100-150 ppm.

HISTORY

Although vanadium mining was known in USA and Peru, for many years, the true potentiality of vanadium failed to be realized till the beginning of the World War-II (1940-1944). During that period the recorded world production maintained itself at a high level reaching a peak of about 4400 tonnes in 1943. However, most of the vanadium came as a byproduct during mining of uranium ore which was in high demand during that period, and as such was not due to a high demand of vanadium itself. Consequent to surplus production vis-a-vis demand, vanadium stockpiles mounted in USA and its production was progressively curtailed. In 1947, the world production was of the order of 1741 tonnes. In the year 1950, very pure vanadium metal (over 99.8% purity, known as '*ductile vanadium*') having wide industrial applications, was made for the first time, and thereafter the production kept increasing. The world vanadium metal production was 632 tonnes in 1960 increasing to 13800 tonnes in 1970 and then reached 41800 tonnes in 1981. After 1981, the production declined and somewhat stabilized. In 1997, it was 35,000 tonnes. In 2000, the production was 59500 tonnes.

In India, although, occurrences of vanadium in association with titaniferous magnetite and with green mica were known long ago, and more recently those in association with bauxite and lignite, there is no large scale commercial exploitation of this metal except byproduct recovery of small quantities from aluminium plants.

RECOVERY

In nature, the vanadium content in its ores is low — generally the V_2O_5 content varying up to 2% or so. Some of the phosphate rocks from which vanadium was recovered in the past as a byproduct, contained as low as 0.3% V_2O_5 . The vanadium-bearing minerals are mined by both underground and opencast methods. The run-of-mine mineral is crushed and ground, mixed with sodium chloride and roasted at 850°C. The vanadium oxides are converted into sodium metavanadate ($NaVO_3$) which is soluble in water. By adding sulphuric acid to this solution, sodium hexavanadate ($Na_2H_2V_6O_{17}$) containing 85–94% V_2O_5 is precipitated, which after drying, is marketed as commercial grade vanadium pentoxide. This is used for making ferro-vanadium (35–55% V), for making chemicals and for direct addition to steel.

To make elemental vanadium, vanadium pentoxide is mixed with calcium metal chips and ignited.

CRITERIA OF USE

Atomic number of vanadium is 23 and its atomic weight 50.9414. It is a medium heavy metal having specific gravity 6.11 (i.e., 22% higher than iron). Its melting point is 1880–1900°C and boiling point 3380°C. The critical properties which particularly determine its important applications are as follows:

- (1) **Mechanical properties:** Pure vanadium metal is soft, highly ductile and malleable. Combination of more and more of certain other elements progressively increases its hardness. In other words, its strength is sensitive to interstitial impurities — 30000 psi in the purest form to 80000 psi in the commercial form containing 85–94% V_2O_5 . It retains strength at elevated temperatures.
- (2) **Chemical affinity:** It readily combines with oxygen and nitrogen. It tends to easily oxidize at a temperature above 663°C, which is the melting point of V_2O_5 . It is very resistant to HCl and H_2SO_4 acids and to salts.
- (3) **Alloyability:** While it easily alloys with many metals and alloys like steel, aluminium-titanium alloy etc, it does not alloy with uranium.
- (4) **Workability:** It can be both hot and cold worked.
- (5) **Thermal conductivity:** It has very low thermal conductivity (10% of copper). Vanadium dioxide has heat-reflective property.
- (6) **Nuclear property:** Vanadium metal has a low cross section of neutron capture — 5 barns only (cf., niobium/tantalum 21 barns).
- (7) **Vanadium pentoxide or V_2O_5 :** This compound is toxic. It is practically insoluble in water i.e., only 0.1 part of V_2O_5 can be dissolved in 100 parts of water; it remains in colloidal solution in water. When cold, its colour is yellow, but with progressive increase in temperature, transforms into brown, ruby red, metallic steel blue and finally into brick red. Solid V_2O_5 has nil electric conductivity. V_2O_5 function is cyclic, so that a small amount of it accelerates oxidation of metals etc., itself being reduced to V_2O_4 only to regenerate back into V_2O_5 by reacting with air.

USES

The special properties of vanadium have made it suitable for a number of industrial uses. These are as follows:

- (1) **Steel:** Vanadium is used as an alloying material for adjusting hardness; for imparting resistance to fatigue, torsion strain and shock; and for increasing ductility. It is introduced into steel in the form of V_2O_5 or ferro-vanadium (Fe-Va). The quantity depends on the properties of steel to be achieved. Only 1.25% is sufficient where resistance of the steel to strain, shock and fatigue is required (e.g., alloy tools), while as much as 4-5% may be necessary if strength (e.g., high speed steel), or ductility (e.g., thin rods or wires) is important.

The characteristic strength and chemical resistance of vanadium, help to increase the resistance of the steel to fatigue, strain, shock and also to HCl, H_2SO_4 acids and salts (e.g., sea water). The ability of vanadium to retain strength at elevated temperatures makes it all the more suitable for this role. Its high ductility and easy alloyability with steel are the other properties made use of in this application.

- (2) **Steel making:** The ability of vanadium to easily combine with oxygen and nitrogen in its molten state, makes it a useful reagent for lowering the levels of oxygen and nitrogen in steel.
- (3) **Alloys:** Ferro-vanadium (Fe-V) containing 50-55% V, 1% (Max) Al and the balance Fe is the most important vanadium-based alloy, and vanadium is added in this form to steel for imparting special properties. another important alloy is '*Titanium 6-4 alloy*', which is a titanium alloy containing 6% aluminium and 4% vanadium which is made use of in supersonic aircrafts in which a very high strength to weight ratio is required. Titanium as such is very light and aluminium is also light. Vanadium is preferred for its strength and its ability to alloy with these metals easily. The other vanadium-bearing alloys are:

<i>Alloy</i>	<i>Composition</i>	<i>Properties/uses</i>
18% tungsten general purpose high speed steel	0.75% C; 4.5% Cr; 18.0% W; 1.25% V	Drills; reamers; lathe tools; broaches; milling cutters; punches; dies.
12% cobalt super high speed steel	0.8% C; 4.5% Cr; 21.0% W; 1.25% V; 12.0% Co	Heavy duty machining on high tensile alloy steel; forged products; close-grained cast iron products; railway coach tires.
Titanium aluminium vanadium alloy	Ti 90%; Al 6%; V 4%	Used in sheet and forgings for airframe parts, and in gas turbine compressor blades.
Titanium vanadium chromium aluminium beta alloy	Ti 73%; V 13%; Cr 11%; Al 3%	Good weldability; high density; thermally stable above 370°C; amenability to cold working. Used in cold-headed bolts.

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- (4) **Nuclear fuel element cladding:** In nuclear power plants, uranium is commonly used as fuel, which is placed in a matrix called *fuel element*. Vanadium is a suitable material for cladding the fuel element, mainly because it does not alloy with uranium – even at the high temperatures generated in the fuel element, and because it has a low cross-section of neutron capture thus contributing to neutron economy in the nuclear reactor. In addition, its easy workability combined with strength and low thermal conductivity also contributes to its suitability.
- (5) **Chemical compounds:** Vanadium pentoxide (V_2O_5) and ammonium metavanate are commonly used vanadium compounds. Small quantities of these are used in paints, glass, printing, fabric dyeing, pharmacy, electrical objects, ceramic glazes etc. In case of paints and dyes, the toxicity of V_2O_5 makes them resistant to insects and fungi, while its colour, water insolubility and nil electrical conductivity makes V_2O_5 suitable in certain applications.
- (6) **Catalyst:** V_2O_5 can be a cheaper substitute of platinum as a catalyst in manufacture of H_2SO_4 and in synthesis of ammonia, because their manufacturing essentially involves oxidation, and V_2O_5 function being cyclic, it first accelerates oxidation, reducing itself to V_2O_4 , and then the V_2O_4 regenerates back to V_2O_5 by reacting with air.
- (7) **Glass:** The heat-reflective property of vanadium dioxide has potentiality for use as a coating on window glass that might be able to allow sun's light to pass through while blocking its heat. It is in R & D stage in the University of London.

ZINC

As has been mentioned in the chapters on copper and lead, there are three base metals commonly referred to as '*base metals*', and zinc is one of them. The most common economic mineral of zinc is sphalerite [ZnS]. Other important minerals are smithsonite [ZnCO₃], hemimorphite [2ZnO.SiO₂.H₂O], zincite [ZnO], willemite [Zn₂SiO₄] and franklinite [(Fe.Zn.Mn)O.(Fe.Mn)₂O₃]. Uni-metal deposits of sphalerite are not common, and it usually occurs in bi-metal lead-zinc deposits (e.g., Zawar and Rampura-Agucha in Rajasthan) and in multi-metal lead-zinc-copper deposits (e.g., Rangpo in Sikkim, Ambamata in Gujarat). The common host rocks may be dolomite, calc-silicate, quartzite or schist. Cadmium is often present in solid solution with sphalerite.

HISTORY

Zinc was known in Egypt in the form of its alloy bronze as long ago as 2200 BC. Romans were familiar with another alloy of zinc i.e., brass, around 200 BC. But during those times, zinc was not known as a metal, and brass most probably came into usage when smithsonite was unknowingly smelted with copper to yield a new alloy, more yellow and more attractive than bronze. Zinc metal as such was discovered in 1520 AD. During the Medieval Period, important centers of zinc mining (along with copper and lead) developed in Spain, Cornwall, Sweden, Saxony, and some areas of eastern Europe. But mining during those times was, by and large, unorganized. First organized mining started in USA in 1720, followed by Europe in 1740. During 1880, the world production of primary zinc metal was estimated at about 260000 tonnes which rose to over 5 million tonnes in 1968 and to about 7.4 million tonnes in 1992.

Although it is known that zinc mines started working in Zawar area of Rajasthan in India during the 14th century, and that zinc was imported by European countries from India and China, the history of organized zinc ore mining in India is not very old. The old mines of Zawar stopped during the great famine of 1812-13, and no attempt was made to revive them till the World War-II (1940-44). In 1942, the utility branch of the Geological Survey of India worked the ancient mines for a short period. In 1945, mining lease for lead-zinc ore of Zawar was granted by the Mewar state to Metal Corporation of India Ltd. Initially the recovery was confined to only lead concentrate and metal. Production of zinc concentrate could start only in 1950, when the first flotation plant was set up. But even then, the concentrate had to be sent abroad for smelting and refining. In 1966, the Metal Corporation of India

Ltd was nationalized with creation of a new public sector undertaking namely, Hindustan Zinc Ltd (HZL), and mining activity started expanding to different areas. But, the first zinc smelter of India was set up in 1967 by another company namely, Cominco Binani Ltd. However, this smelter located in Alwaye, Kerala processed imported concentrate. The first smelter based on indigenous concentrate was set up by HZL at Debari, Rajasthan in 1968, marking the beginning of recovery of zinc metal from the indigenously mined ore. Recently, the public sector corporation HZL has been privatized, but the name remains unchanged.

The production history of primary zinc in India is as follows:

<i>Year</i>	<i>Production</i>
1967	2991 tonnes
1970	23415 tonnes
1980	43628 tonnes
1990	79093 tonnes
April, 2000-March, 2001	178015 tonnes

RECOVERY

Zinc ores are not directly salable or usable. The ores are first concentrated, and then the zinc concentrate is converted to metal by first roasting and then distillation or electrolytic refining.

Since zinc ores are seldom uni-metal and they commonly contain other metals like lead, copper, cadmium etc., complex techniques of differential flotation are employed for obtaining zinc concentrates. In the first stage, zinc and iron (pyrite) are depressed and separated from lead and copper which are floated. In the next stage, iron is depressed while zinc is floated and recovered as concentrate. The zinc metal content in the Indian ores commonly vary from 3-15%, and the concentrates recovered from these ores contain 50-62% zinc in the form of ZnS. The concentrate is then roasted or calcined to eliminate most of the sulphur and convert the ZnS to impure ZnO.

The next stage is to convert the roasted concentrate to metallic zinc, and this can be accomplished by distillation or electro-winning.

- (a) *Distillation*: This is done in retort plants. ZnO is heated with coal or coke. Zinc having low boiling point at only 907°C, vaporizes, and a mixture of zinc vapour and CO gas is collected in condensers where zinc vapour condenses to liquid zinc metal which is then cast into slabs. Further refining of this zinc metal may be carried out by fractional distillation.
- (b) *Electro-winning*: In this process, the roasted zinc concentrate is leached with dilute sulphuric acid to form ZnSO₄ solution. Some manganese dioxide is added to the leaching solution to oxidize the iron from ferrous to ferric. This solution is subjected to electrolysis with aluminium cathodes and lead-silver anodes in electrolytic cells, where metallic zinc is deposited on aluminium cathodes. The zinc is then scraped off, melted and cast into slabs. Zinc metal thus recovered, can be refined to a high commercial grade of above 99.995% purity.

CRITERIA OF USE

Zinc metal has a unique combination of several physical properties and economic factors. If some of the criteria are considered singly, then copper, aluminium, lead and tin may be superior to zinc. But if all the properties are considered in combination, then amongst the common metals it will be difficult to find a parallel of zinc, and there are some industrial applications in which this combination of properties becomes crucial criterion. The principal criteria are as follows:

1. Thermal properties:

- (i) Zinc has a relatively low melting point of 420°C , which is, though, higher than that of lead (327°C) and tin (232°C), is much lower than that of copper (1083°C) and aluminium (660°C). Consequently, zinc is fairly easily castable.
- (ii) The boiling point of zinc is very low, being only 907°C (cf., lead: 1740°C , tin: 2270°C , aluminium: 2494°C , copper: 2595°C). This low boiling point facilitates refining of zinc metal by distillation.
- (iii) Molten zinc possesses a high degree of fluidity.
- (iv) Cooling of molten zinc is very smooth, associated with practically no shrinkage on solidification and no change in mechanical properties.
- (v) Zinc is a fair conductor of heat (25% that of silver).
- (vi) When ignited, zinc spreads a green glaring cloud with spreader stars.

2. Mechanical properties:

- (i) Zinc is soft and malleable, and at the same time has higher tensile strength than lead which is also very soft. Malleability of zinc increases on heating.
- (ii) Though its specific heat is fairly high— 7.13, it is much lower than that of lead (11.34 at 16°C).

3. Colour and lustre: Zinc is a lustrous metal having a brilliant bluish white colour.

4. Electrical and electrochemical properties:

- (i) Zinc is a fair conductor of electricity – 25% that of silver which has the highest conductivity amongst all metals (cf., iron 16%, aluminium 57%, copper 94%).
- (ii) Position of zinc in the electrochemical (or electromotive series) is lower than that of a number of metals including iron. In other words, zinc dissolves in an aqueous electrically conductor liquid (e.g., H_2SO_4 acid) more easily than iron, and in the process, gains more electrical energy by acquiring higher positive charge than iron.

5. Chemical and alloying properties:

- (i) It has relatively weak affinity for oxygen.
- (ii) It is resistant to atmospheric corrosion due to its weak affinity for oxygen.
- (iii) It can form alloys easily. The common alloying agents are copper, aluminium, magnesium, tin.

6. Economic factor: Zinc is relatively abundant in nature and consequently cheaper compared to copper, lead and tin.

USES

1. Die casting: Although 'die' signifies a permanent metallic mould, all types of castings in such moulds are not called 'die casting'. For example, when molten metal is just poured into the mould by gravity, the cast is called '*permanent mould casting*'; and if the metal is forged within the mould in a hot plastic state, the casting is called '*hot pressed*' or '*die pressed*' forging. In contrast to these, in die casting, the metal is in a liquid state and is forced into the die under high pressure. This particular technique of casting imparts certain properties to the product, such as uniformity in the degree of compactness and strength, accuracy in shape and dimensions, smooth surface free from pits, absence of any trapped air bubble etc. Consequently, the technique of die casting is particularly suited for yielding products like very intricately shaped objects and machinery parts. The common products of zinc die casting include carburetors, speedometer frames, door handles, pumps etc.

All metals are not amenable to die casting, but zinc is very amenable and popular due to the following reasons:

- (i) Low melting point facilitates easy and inexpensive melting.
- (ii) High fluidity of liquid zinc facilitates smooth unhindered flow of the molten metal of the molten metal into all the nooks and corners inside the die cavity under relatively low pressure, which reduces the cost further.
- (iii) This combination of low temperature and low pressure of the molten metal makes possible the use of relatively inexpensive dies made of ordinary steel. Even such ordinary dies do not wear out quickly. This again contributes to the lowering of the cost of casting.
- (iv) Smooth cooling of molten zinc unattended by shrinkage makes the surface of the product free from pits and cracks, and the product needs practically no subsequent machining or finishing.
- (v) Even when some minor finishing is required, malleability of zinc facilitates that.
- (vi) Tensile strength of zinc is fairly high.

For die casting, very high purity zinc is required. Lead, cadmium, tin, iron and titanium are highly deleterious due to the following reasons :

Lead: High density renders molten lead less fluid than zinc. Also, its lower melting point causes it to solidify later than zinc on cooling, thus affecting the quality of the product of die casting. Further, lead having greater affinity for oxygen, its grains getting into the product may tend to react with oxygen on exposure to warm moist atmosphere.

Cadmium: Lower melting point causes late solidification.

Tin: lower melting point causes late solidification. Also, it shrinks in volume to the extent of 2.8% on cooling.

Titanium: Highly refractory and difficult to melt.

Iron: Its melting point is higher than that of zinc, and a high content of iron will not suit a die made of steel.

The specifications usually preferred are: 99.99% (min) Zn; 0.005% (max) Ti + Fe + Pb; 0.004% (max) Cd; 0.003% (max) Sn.

2. Galvanizing: The word 'galvanizing' has become synonymous with zinc coating. Strictly speaking, this term should be associated with electricity, and perhaps the original practice of zinc coating by electrolysis was signified by it. But now, applying a coating of zinc on the surface of iron body by any method is called galvanizing. It may be effected by any of the following four methods:

- (i) Depositing zinc electrolytically on the surface (electrogalvanizing).
- (ii) Immersing the body in molten zinc (hot dip process).
- (iii) Spraying the surface with molten zinc.
- (iv) Exposing the surface to zinc vapour or to finely powdered zinc at a temperature near its melting point (sherding).

Coating of zinc serves to protect iron sheets against corrosion. Zinc is preferred in this application due to the following reasons:

- (i) The brilliant colour and luster of zinc imparts a beautiful finish to the coated surface.
- (ii) Zinc itself is resistant to atmospheric corrosion in the short run.
- (iii) Even on long exposure to atmosphere, zinc on account of its affinity for oxygen, forms oxide which then reacts with CO_2 to form ZnCO_3 . This being resistant to further reaction, serves to save the iron body from corrosion.
- (iv) Low melting point, low boiling point and relatively easy availability of zinc render the whole process very economical.
- (v) Between lead and zinc, the latter is preferred because its specific gravity is much less and consequently, it increases the weight of the galvanized sheet to a lesser extent.

Chemically, iron is regarded as a deleterious constituent in zinc, because it tends to increase the melting point of zinc. Generally, a maximum limit of 0.5% Fe is specified.

3. Rolled products: Zinc being soft and malleable can be conveniently rolled into thin sheets, and then cut and fabricated into various shapes. Further, rolling of hot slabs is all the more facilitated, because malleability of zinc increases on heating and subsequent cooling does not alter the mechanical properties. Rolled products of zinc include jar caps, dry cell cans etc.

4. Alloys:

- (a) *Brass:* The most important zinc-based alloy is brass. The important types of brass are:

<i>Name of brass</i>	<i>Composition</i>	<i>Properties/Uses</i>
(31) High tensile brass	Cu 55%; Zn 38%; Al 2%; Fe 2%; Mn 3%	Used where high-strength castings are required, as in marine propellers.
(32) Die-casting brass	Cu 60%; Zn 39.5%; Al 0.5%	Used for general purpose die-casting works.
Brass	75% Cu; 21% Zn; 3% Pb; 1% Sn	Suitable for valves, pressure tight castings, plumbers' fittings, ornamental castings.
Naval brass	62% Cu; 36.75% Zn; 1.25% Sn	Good resistance to corrosion in salt water. Used in the form of sheets and extrusions.

In brass, lead is added to improve machinability. But US and Canadian restrictions on lead content in potable water setting the limit at 15 ppb at the tap, has forced manufacturers to go for lead-free brass for use in potable water pipe line fittings. A new kind of brass called '*SeBiLOY*' was developed by replacing lead with selenium and bismuth. This alloy is now known as '*EnviroBrass*'. Depending on usage, its composition varies as: 4-38% Zn; 6%(Max) Sn; 0.5-2.2% Bi; 0.01-1.1% Se; 0.5% (Max) Fe; 0.25% (Max) Pb; 1.0% (Max) Ni; 0.25% (Max) Sb; 0.05% (Max) P; 0.6% (Max) Al; balance Cu. Selenium and bismuth contribute to machinability.

(b) *German silver or nickel silver*: This is not silver, and is an alloy containing mainly copper, nickel and zinc. It is called so because of its bright silvery appearance. There are three varieties:

- 10% nickel silver containing 62% Cu, 10% Ni and 28% Zn; it is used in the form of sheet and strip for production of cutlery, tableware and decorative articles.
- 18% nickel silver containing 55% Cu, 18% Ni and 27% Zn; it is used for making springs and contacts in telecommunication equipment.
- machinable quality nickel silver containing 46.5% Cu, 9.5% Ni, 41.25% Zn and 2.75% Pb; it has good machinability and can be machined into non-standard shapes for making various decorative objects.

(c) *Magnesium-based structural materials*:

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
Magnesium-96	96% Mg; 2.5–3.5% Al; 0.7–1.3% Zn; 0.2% (min) Mn; 0.3% (max) Si	Sheet, plate, press-forgings, aircraft, guided missile parts, aircraft and car wheels.
Magnesium-92	92% Mg; 5.8–7.2% Al; 0.4–1.5% Zn; 0.15% (min) Mn; 0.3% (max) Si	Extruded bars and tubes, forgings.
Magnesium-90	90% Mg; 5.3–6.7% Al; 2.5–3.5% Zn; 0.5% (max) Mn; 0.3% (max) Si; 0.1% Cu	Sand-casting for use in aircraft and in machine parts for textile and packaging industries.
Magnesium-89	89% Mg; 8.3–9.7% Al; 0.4–1.0% Zn; 0.13% (max) Mn; 0.5% (max) Si; 0.1% Cu	Die-casting for use in pumps, portable tools etc. for operation under light pressure conditions.

(d) *Damascene work*: Damascene work is an art of metal ornamentation. It has been defined Sir Gregory Birdwood as the “art of encrusting one metal on another not in pieces which are soldered or wedged, but in the form of wire which, by undercutting and hammering, is thoroughly incorporated the metal which it is intended to ornament. The best living example of this work is the '*bidricraft*' or '*bidriware*' of Bidar in Karnataka, India, after which it is named. This craft is the Indian adaptation of the '*koftgari*' work of Iran brought to India in 13th century. In this craft, gold or silver wire is encrusted on a metal body cast in a mould by the lost wax process (for details see bronze in the chapter on copper). The metal used in bidriware is copper and zinc in 1:16 proportion.

(e) *Other alloys with zinc :*

<i>Name of alloy</i>	<i>Composition</i>	<i>Properties/Uses</i>
“Ashtadhatu” or alloy of eight metals	Au, Ag, Cu, Pb, Sn, Fe, bronze and brass	This was first made during the prehistoric era, by mixing all the metals and their alloys that were known and available then. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship.
“Panchadhatu” or alloy of five metals	Alloy of Sn, Cu, Pb, Fe and brass	This is one of several types of “Panchadhatu” first made during the prehistoric era. Considered very auspicious in Hindu scriptures, and is used for casting icons for worship. It is a cheaper version of “Ashtadhatu” sans gold and silver.
Aluminium-zinc-silicon-nickel-magnesium	Si, Ni, Mg added in a matrix of Al-Zn	Used in light alloy crankcases of vehicle engines.
Gunmetal or Admiralty bronze	88% Cu; 10% Sn; 2% Zn	Corrosion resistant in marine conditions. Used in general utility construction parts.

- 5. Chemical compounds:** Common compounds of zinc include zinc oxide, leaded zinc oxide, lithopone, zinc chloride and zinc sulphate. These are used in paints, medicines, rubber, textiles, paper etc. ZnO_2 is used as a filler to improve the quality of titanium dioxide pigment. This pigment tends to yellow over a long duration of time, and to increase durability, it is used in combination with 5–20% of ZnO_2 . In rubber used in car tyres, application of small doses of ZnO increases the effectiveness of vulcanization process (i.e., the process of treatment of rubber with sulphur). Zinc sulphidosilicate is a fluorescent substance and used in the inner wall of fluorescent tubes.
- 6. Oil drier:** Oil, paints and varnishes dry by the uptake of oxygen. The exact mechanism by which the drying takes place, is not known. But it is believed that the unsaturated fatty acids in oils make them reactive and they attract great amounts of oxygen causing polymerization. This ability of unsaturated oils make them form a solid, coherent and adherent film when spread on a surface and exposed to air. Normally, this process of oxidative polymerization is slow taking 12–36 hours. Various driers called siccatives, are, therefore, added to them to accelerate this process. Zinc sulphate can be used as a drier.
- 7. Dry cell:** This is a primary or non-rechargeable cell. In this application, zinc is used mainly on account of its electrical conductivity and its much lower position in the electrochemical series in relation to certain other elements like carbon, copper etc. Zinc serves the purpose of the negative electrode while carbon or copper, that of the positive electrode. In the voltaic cell, copper and zinc rods are immersed in dilute sulphuric acid. In the Leclanche cell, carbon rod is dipped in ammonium chloride solution while the container itself is made of zinc which serves as the negative electrode. Electric current flows as soon as the two electrodes are connected and the circuit completed.

8. **Alkaline battery:** This is also a primary or non-rechargeable battery. The positive pole (anode) contains zinc, while the negative pole (cathode) contains manganese dioxide. The electrolyte used is a strong alkali like potassium hydroxide or sodium hydroxide.
9. **Gold recovery:** In the cyanidation process of gold recovery, the zinc dusts are added to the cyanide solution containing gold and silver to aid their precipitation. Later on, by melting, zinc is easily driven off as vapour, and gold and silver are recovered. In this application, the low boiling point of zinc is the key to its preference.
10. **Human diet:** Inclusion of trace amounts of zinc in food is necessary for human health. Zinc-coated proteins help formation of insulin. Deficiency of zinc tends to retard growth and to cause anemia. It also plays an important role in the formation of protein in the body, in wound healing, in blood formation and in general growth and maintenance of all tissues. Thus it is involved in most of the metabolic processes. It enters the system of human body from soil through plants and vegetables.
11. **Pyrotechnics:** The green cloud with stars produced by zinc on ignition, is made use of in giving attractive effects in fire works.

WASTE UTILIZATION

Wastes generate during and after processing as well as after use of consumer products. Some of the wastes can be recovered.

1. **Recovery of sulphur:** Sphalerite contains 67% Zn and 33% S. Thus its sulphur content is much higher than that of galena (13.4% S) and is comparable with that of chalcopyrite (35% S). This sulphur, which is eliminated during roasting of the concentrate, is recovered in the form of sulphuric acid.
2. **Moore cake or residues after distillation and leaching:** As has been described in this chapter, there are two routes for recovery of zinc. The roasted concentrate may either be leached with dilute sulphuric acid to dissolve the zinc in the form of $ZnSO_4$ for subsequent electrolysis, or be retorted for distillation of zinc. The residues left after leaching or distillation are called '*Moore cake*'. It may contain zinc values and also lead, gold and silver. These valuable metals are recovered by treating the residue in lead smelter.
3. **Recycling:** In the past, recycling of zinc scrap used to be negligible. This was because of two main reasons. Firstly, zinc ore being relatively abundant, sufficient primary zinc itself was available. Secondly, in the electrochemical series, the common alloying metals like iron, tin, lead etc. occupy higher position than zinc and lower position than copper. This signifies that in a solvent, zinc dissolves more readily than these alloying metals and so cannot be recovered easily, while copper being less soluble compared to them, can be recovered more easily.

However, the scenario has changed considerably in the recent past, even though it is much less than copper and lead. According to an estimation made in 1992, the recycling rate (it is defined as the ratio of the annually utilized quantities of scrap to the annual production of primary metal) of zinc scrap was 29% in Western Europe (cf., copper 50%, lead 55%), 27% in USA (cf., copper 60%, lead 59%), and 20% in Japan (cf., copper 47%, lead 38%). In this recycling, share of new scrap far exceeds that of old scrap. New scrap is that scrap which is generated during fabrication of zinc products, while old scrap comprises the used zinc fabrication products. Until recently, die-castings and brass and bronze objects mainly

contributed to the recyclable old scrap. But presently a new trend is emerging due to the increased processing of galvanized steel scrap in electric arc furnaces for recovering secondary iron. The dust generated in these furnaces contain significant quantities of zinc which defies reclamation by conventional technology. New technologies involving plasma furnaces are gaining relevance for recycling of the zinc used in galvanizing of iron and steel sheets. It has been claimed that a unique hydrometallurgical process developed in Italy can economically extract high purity zinc metal from various zinc-bearing waste residues such as galvanizing ashes, zinc and brass foundry fumes, electric arc furnace dust and zinc carbonates.

4. **Micronutrients for soil:** Zinc in the form of zinc sulphate is added to chemical fertilizers as a micronutrient, which is essential for crop growth. For this purpose, very finely divided zinc skimming and zinc ash containing zinc oxide are used. Such skimming and ash are generated as wastes from zinc smelting industry.
5. **Copper cake:** Copper cake is generated as a result of copper-cadmium purification of the zinc sulphate solution. Copper cake contains about 50% Cu and 10-20% Zn. Researches have indicated that copper cake can be used as a reagent for purification while in the process, the zinc can be recovered as sulphate. Also, there is good potentiality of extracting the copper by solvent extraction followed by electrolysis of the copper solution.
6. **Cobalt cake (beta cake):** Cobalt cake is another residue generated during purification process. It contains about 30% Zn, 1% Co, 7% Cd, 10% Cu and 1% Ni. It has been found possible to recover zinc by solvent extraction process, but cobalt and nickel may be difficult to separate and recover.
7. **Gypsum residue:** All zinc concentrates contain calcium in varying proportions. This calcium is removed from the system in the form of gypsum. But this gypsum causes reduction in current efficiency and may also get deposited in the pipelines. It contains about 20% Zn and so is not marketable as such. Moreover complete recovery of zinc from this gypsum may create operational problems. But it may be possible to recover a part of the zinc as indicated by laboratory scale researches.
8. **Anode wash residue:** As has been mentioned earlier in this chapter, during eletro-winning process some manganese dioxide is added to the leaching solution for oxidizing the iron present. Some residual manganese remains in the electrolyte. On electrolysis, oxygen is liberated at the lead-silver anode and this oxygen reacts with the manganese to form manganese dioxide. The MnO_2 -bearing residue obtained by this process is called '*anode wash residue*' which contains about 55% MnO_2 . This residue can be recycled back into the leaching solution for oxidizing iron.

SUBSTITUTION

It has not been possible to find a substitute of zinc for making brass although certain consumer products made of it are giving way to those made of aluminium and stainless steel. Similarly zinc enjoys a decisive cost advantage in galvanizing of iron and steel; but the galvanized steel sheets are themselves are in some cases being replaced by aluminium depending on the costs and benefits. Another field of use where zinc-based consumer products are being substituted is the dry cell. The conventional zinc-carbon dry cells are now giving way to more efficient, though more expensive, alkali cells.

In die casting, the possible rivals of zinc could be lead, tin, aluminium and copper. The merits and demerits are as follows:

- (i) Lead: Although its melting point is lower and consequently, its melting cost is also lower than that of zinc, it is heavier and more viscous in molten state and also it has lower tensile strength.
- (ii) Copper: Melting point is very high and consequently, melting cost is higher than that of zinc. Further, its high melting point requires dies made of special and more expensive material than ordinary steel. Also, copper itself is more expensive than zinc. On the other hand, copper is good conductors of heat and electricity, and some products may require these qualities.
- (iii) Aluminium: Its high melting point increases the cost of melting and also that of the dies which are required to withstand high temperature. However, at the same time, it is light, strong, highly resistant to corrosion and good conductor of electricity. It is, therefore, preferred to zinc in die casting of certain objects – particularly some of those used in structural works and electrical equipments.
- (iv) Tin: Melting point is lower than that of zinc and shrinkage on cooling is also very low (2.8%). It is very expensive, and hence, is suitable for die casting of expensive intricate parts requiring high degree of precision.

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SECTION - 3

METALLOIDS

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ANTIMONY

Antimony has been known to be in use since as long ago as 4000 BC. There is record of its knowledge and usage during the Egyptian civilization and the biblical times. It is a metalloid having some properties typical of metals but also the characteristic brittleness of nonmetallic elements. Stibnite (Sb_2S_3) is the only commercial source mineral. It theoretically contains 71.4% Sb. It is also recovered as a byproduct of lead-zinc mining.

In India, the mining history goes back to 1905, when a small quantity of its mineral stibnite along with its decomposed products was mined in Lahul area of Himachal Pradesh on trial basis, and was sent to England for processing. However, due to the high altitude (over 4000 m), inclement climate and inaccessibility of the area during most part of the year, exploitation of the deposit remained a nonstarter. Presently, there is no production reported in India. China, Russia and South Africa are the main producers accounting for about 90% of the total world production of 120000 tonnes during 2000.

Stibnite is an easily fusible mineral. On melting and preliminary treatment of the molten mineral, crude antimony containing 70% Sb is obtained. From this, first the unrefined metal called '*regulus*', and then the refined metal called '*star antimony*' containing over 99% Sb are obtained.

CRITERIA OF USE

Antimony metal is very hard, brittle and normally silvery white in colour. But when electrically or chemically deposited from an antimony solution as a fine powder, the colour of the metal is black, and it is known as '*antimony black*'.

Elemental antimony may be in two allotropic forms – alpha and beta. The alpha form is extremely unstable and very sensitive to heat, and even a mechanical scratch may transform it into beta form with sudden generation of heat.

A peculiar property of antimony metal is that it slightly expands (instead of contracting) on cooling. Its melting point is 630°C.

Antimony forms chemical compounds with sulphur (Sb_2S_3 , Sb_2S_5), chlorine (SbCl_3) and oxygen (Sb_2O_3). These compounds have different colours ranging from white to black. Besides, it forms some organic compounds also. The compound SbCl_3 has a tendency to fume easily. The compound Sb_2O_3 has a relatively high refractive index of 2.09 (cf., value for glass 1.52).

USES

- 1. Alloys:** The commonest use of antimony metal is in the form of an alloy with lead. Lead is too soft to be used alone in many of the applications. On the other hand, antimony, though hard, is too brittle to be used alone. An alloy of the two metals makes an ideal material in many applications, such as in storage battery plates, sheets, pipes, sheathing of electrical cables, bullets, tooth paste tubes etc. Another advantage is that the casting of the alloy does not involve change in size, because, on solidification, molten lead tends to contract in size whereas molten antimony tends to expand. The antimony content in such alloys may range from 1-11 percent. The lead-based metal used in bearings, known as '*white metal*' may contain up to 15% antimony.

Antimony may also form alloys with tin, copper etc. '*Type metal*' used by printers is an alloy containing mainly lead, tin and about 30% antimony. '*Pewter*' is a tin-copper-antimony alloy known since the Roman Era for use in household articles. '*Britannia metal*' is a tin-antimony alloy containing small amounts of copper, zinc, lead and bismuth. Tin-based white metal or '*Babbitt metal*' containing 88.25% (min) Sn; 3-4% Cu; 7-8% Sb; 0.5% Pb is used in automobiles and engineering works.

The relatively low melting point of antimony makes it a suitable alloying metal with uranium for use in reactors operating on liquid fuel.

- 2. Pigments:** Natural stibnite powder – '*Surma*' is brownish black coloured and is used as a cosmetic for application to eyes and eyebrows. Another compound — Sb_2S_3 , prepared by treating a solution of antimony salt with sulphureted hydrogen, is red coloured and is called '*antimony vermilion*'. Antimony oxide is white coloured and is called '*antimony white*'. '*Antimony yellow*' is produced by slow oxidation of the sulphide. '*Antimony blue*', '*antimony violet*' etc. are produced by mixing antimony yellow with other pigments. The chloride SbCl_3 is brown coloured. '*Antimony black*' obtained as a fine powder chemically or electrolytically from an antimony solution, can be used as a black colouring material.
- 3. Smoke production:** The key criteria are the extreme instability of alpha antimony and the tendency of SbCl_3 to fume. When SbCl_3 is electrolyzed, the alpha antimony is deposited and thus a solid solution of alpha antimony and SbCl_3 results. This solid solution is known as '*explosive antimony*'. When the alpha antimony is hit or scratched, it readily transforms into beta antimony generating heat due to which dense clouds of SbCl_3 is formed. This phenomenon is made use of in shrapnel, sporting guns, smoke bombs etc.
- 4. Enameling:** In ceramics, Sb_2O_3 is used as an opacifier in enamels. The white colour of the oxide and its high refractive index are the key parameters.
- 5. Fire resistant material:** Carbon tetrachloride, carbon dioxide etc. are common chemicals used for extinguishing fire. The principle is to cut off oxygen and cool down the temperature of the material in fire. In the manufacturing of fire-resistant fabric for use in military or of fire-resistant plastic, a mixture comprising Sb_2O_3 and chlorinated paraffin or

SbCl_3 in an organic solvent is used as a coating material along with Na_2CO_3 solution. The heat of fire triggers off instant chemical reactions to produce the necessary chemicals and the necessary conditions to extinguish the fire.

6. **Synthetic marble:** Synthetic marble is made by casting and heat-curing (in presence of a catalyst) a mixture of alumina and resin matrix with some filler material. The filler constitutes 50-85% of the weight of the mixture. Antimony oxide is used as a filler when the synthetic marble is used in bathroom tiles and structural components. High refractive index (for opacifying effect) and white colour are the main criteria.
7. **Pyrotechnics:** A mixture of powdered antimony (200-300 mesh size), potassium nitrate and sulphur is used in fire works. The antimony produces a white fire with glitter effect.
8. **Other uses:** Sulphides of antimony are used for vulcanizing rubber. Compounds of antimony have medicinal properties. tartar emetic and potassium antimony tartarate are used as mordant in dyeing. Sb_2S_3 is used to the extent of about 3% in heads of safety matches, and to the extent of about 8% in the striking surface of the match boxes.

ARSENIC

Arsenic is a metalloid. Arsenopyrite ($\text{FeS}_2 \cdot \text{FeAs}_2$), realgar (AsS) and orpiment (As_2S_3) are the most common natural sources of arsenic. In the 9th century, an alchemist named Geber while experimenting with different materials in search of copper, burnt realgar and obtained a white tasteless powder which he called arsenic. It was actually arsenic oxide. All through history, this substance has been commonly referred to as arsenic which is, however, a different material altogether. Arsenic is hard, brittle and highly poisonous. Its hardness is a typical characteristic of metals while brittleness that of nonmetallic elements.

Being very brittle, arsenic is not used in its elemental form. Its alloys and compounds find a variety of applications as follows:

1. **Alloys:** Addition of 0.1-0.5% arsenic to copper makes the latter harder with stronger resistance to heat and corrosion. Alloy of lead containing 1% As hardens lead and is used in lead shots. The alloy antimony-tin-lead-arsenic serves as a good solder, the role of arsenic being to produce a fine texture.
2. **Compounds:**
 - (i) *Poison:* The highly poisonous nature of arsenic makes some of its compounds suitable as insecticide ('white arsenic' or arsenous oxide), bactericide in preservation of timber, hide, leather etc. (sodium arsenite, arsenates of lead and calcium), chemical warfare ('lewisite' or chlorovinyl dichlorarsine) and weed killer. Arsenous oxide dissolves easily in water forming arsenous acid which is a fatal poison for human beings. It was popular as a *fashionable murder weapon* used by royal successors (that is why its another name was *powder de succession*).
 - (ii) *Paint:* Orpiment is a golden paint used in lacquer works. Orpiment mixed with indigo yields green tints. Realgar is orange red pigment.
 - (iii) *Medicine:* The bacteria-killing ability makes arsenic compounds like arsenates of lead and calcium suitable in medicines for external use, such as medicinal bath soaps.
 - (iv) *Other uses:* White arsenic is used in opalescent glass making, and in calico printing as a mordant of dyes. Orpiment can be used as a hair remover.

BISMUTH

Though bismuth is known to be used during the Medieval Period, it was identified as an element for the first time during 18th century. It is actually a metalloid with some properties (*e.g.*, brittleness) resembling those of a nonmetallic element, and some others like metals. Its incidence in the earth's crust is hardly 1 ppm. It may occur in nature as a native element or in sulphide form *i.e.*, bismuthinite (Bi_2S_3), which commonly weathers to bismuth ochre or bismite ($\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). The other minerals of bismuth are not of economic significance.

CRITERIA OF USE

Bismuth is a silvery white substance with pinkish tinge. It is hard and brittle. Its specific gravity at 20°C is 9.80. It has a relatively low smelting melting point of 271°C. But one of its most characteristic properties is that in molten state, its specific gravity is higher, and on solidification it expands by 3.32% instead of contracting. The other most characteristic property is that its alloys melt at lower temperature than any of the individual component metals. It has a smooth feel. Its thermal conductivity is less than that of any other metal except mercury, being only 0.018 cal/sec/cm³ at 100°C.

USES

- 1. Alloys:** Bismuth is necessary for manufacturing characteristically low melting alloys. The property of bismuth alloys to have low melting point than component metals is the key to this application of bismuth. Another advantage is the power of expansion of bismuth on solidification. As a consequence of this, the alloys do not tend to shrink on solidification (shrinkage of other metals is offset by expansion of bismuth). Also, such alloys are hard and heat resistant due to the hardness and low thermal conductivity of bismuth. The common alloying metals are lead, cadmium, tin, antimony, copper, aluminium etc. Some common alloys are as follows:
 - (i) Wood's metal : It contains 50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd; it melts at 70°C.
 - (ii) Rose's metal : It contains 50% Bi, 25–28% Pb, 22–25% Sn; it melts at 94°C.
 - (iii) Lipowitz's alloy : It contains 50% Bi, 27% Pb, 23% Sn.
 - (iv) Newton's metal : It contains 50% Bi, 31.25% Pb, 18.75% Sn.

2. **Automatic water sprinklers and safety plugs:** In this application, an alloy containing Bi, Sn and Cd is used. This is the lowest melting alloy having melting point 60°C *i.e.*, it can melt in hot water or even in a hot room. This characteristic makes it an ideal material in automatic water sprinklers for protection against fire. In such a sprinkler, there is a lid made of this bismuth alloy which melts away as soon as the room becomes hot due to fire, and water starts flowing out. Similar principle also works in case of safety plugs.
3. **Rust-proof temporary coating:** The low melting points of bismuth-based alloys make them suitable materials for coating metal tools during transit in order to prevent rusting. At the time of use, the tools are simply washed with hot water to melt away the coating.
4. **Nuclear fuel:** Uranium-bismuth alloy, on account of low melting point, find use in atomic reactors as liquid fuel.
5. **EnviroBrass:** Brass is an alloy of copper and zinc to which lead (3-9%) is added to improve machinability and achieve pressure tightness. This brass is used in water pipeline fittings. But recently in USA and Canada, limit of lead content in potable water has been set at 15 ppb. A new type of lead-free brasses called '*SeBiLOY*' which has later been renamed as '*EnviroBrass*', has been developed. In this alloy lead-content is limited to 0.25% and instead bismuth (0.5-2.2%) and selenium (0.01-1.1%) are incorporated. While selenium improves machinability, bismuth serves to add strength and pressure tightness.
6. **Chemical compounds:** Important compounds of bismuth are: trioxide, hydroxide, trichloride, subcarbonate, subchloride, subiodide, nitrate etc. these chemicals find use in pharmaceutical, chemical, cosmetic, glass and porcelain industries.
7. **Superconductor:** National Physical Laboratory, India, in the 1990s carried out investigations with silver-sheathed wire based on bismuth oxide. This combination was found to hold potentiality as a high temperature superconductor.

BORON

Boron is a metalloid, i.e., it belongs to the border line between metals and nonmetals. In certain respects it behaves like metals, and some of its characteristics are like those of nonmetals. Boron is recovered from boric acid [H_3BO_3], which in its turn is produced from minerals like borax [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$], kernite or rasorite [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$] or from natural brine water.

Although borax is known for centuries (the earliest record dates back to 1563), the element boron was first isolated by Sir Humphrey Davy (UK) in 1807 by electrolysis, and by Louis-Jacque Thenard (France) in 1808 by reduction. Hemi Moissan succeeded in purifying boron to above 98% grade. But its commercial production remained a nonstarter till the later half of 20th century. Its end-uses were by its incorporation into other metals through its compounds.

In the pure elemental boron, there are two isotopes namely B^{10} and B^{11} , the former making up 19.78% and the latter 80.22% of the total boron.

RECOVERY

Boron is difficult to recover because of its strong reactivity with both oxygen and nitrogen, and its extraction has to be done in inert atmosphere or in vacuum. Boric acid [H_3BO_3] is converted to boric oxide [B_2O_3] by calcination. Boric oxide is reduced to boron by pyrolysis or reaction with magnesium metal at high temperature of the order of 2000°C (the melting point of boron is 2079°C). To obtain high purity boron, the impure element is degassed in vacuum. The two isotopes of boron namely B^{10} and B^{11} are separated by fractional distillation or by diffusion at above 2550°C, which is the sublimation temperature of boron.

CRITERIA OF USE

1. **Form:** Boron may be either crystalline or amorphous.
2. **Mechanical properties:** It is hard and it retains its strength at high temperatures.
3. **Chemical reactivity:** It is extremely reactive at high temperature with oxygen and nitrogen. Amorphous boron burns with a distinct green flare.
4. **Electrical/thermal conductivity:** It behaves like a nonmetal inasmuch as it is an electrical insulator, but it conducts heat like a metal. Recently, however, it has been discovered that it is not totally nonconductive to electricity, but is a semiconductor (materials with resistivity intermediate between metals and insulators).

5. **Neutron absorption:** B^{10} is capable of absorbing neutrons without emitting gamma rays, while B^{11} has low neutron absorption ability.
6. **Specific gravity:** It is light compared to many metals, having specific gravities 2.34 (crystalline type) and 2.37 (amorphous type).
7. **Melting/boiling point:** Its melting point is high — 2079°C , and it boils and sublimates at 2550°C .

USES

Traditional and some new uses are based on natural borax, and its derivative compounds boric acid and boron oxide. Such industrial uses are outside the scope of this book. So far as the uses of elemental boron is concerned, the important ones are as follows:

1. **Ferroboron:** This is the most common use of boron. This alloy contains 15-20% B and the balance Fe. Boron acts as a hardening agent imparting high strength at elevated temperature. In ferrous metallurgy, boron, by virtue of its strong affinity for oxygen and nitrogen, is used for degasification. It is added in the form of ferroboron.
2. **Nuclear reactor:** Nuclear reactor houses the fuel elements, which contains a matrix supporting the nuclear fuel. Heat is generated within this fuel element due to chain emission of neutrons from the fissionable atoms of the nuclear fuel. The function of a reactor is primarily (i) to contain the dangerous radioactive emissions, and (ii) to prevent loss of the heat generated within it. For this purpose neutron-absorbing shield are provided. Within a reactor, mechanisms are provided to regulate the generation of heat depending upon requirements. For regulating the heat, control rods called “moderators” that are capable of absorbing neutrons, are used. If the rods are lowered down in the reactor, more neutrons will be absorbed and the process of fission will slow down, thus reducing the heat. On the other hand, if the rods are pulled up out of the reactor, then less number of neutrons will be absorbed, and consequently the process of fission will accelerate, thus increasing the heat.

Ability of the isotope B^{10} to absorb neutrons without emitting gamma rays and also its resistance to the heat generated within the reactor, makes it suitable for use both as a moderator and (combined with aluminium or plastic) as a shielding material. In the latter application, its low specific gravity is an added advantage as the shield remains light weight.

The fuel element itself, in contrast, must not contain any neutron-absorbing matrix, because its function is to sustain chain fission. An alloy of uranium with the isotope B_{11} which has low neutron absorption, is suitable as a matrix in some types of fuel element.

3. **Neutron-detecting instruments:** The isotope B^{10} , is used in such instruments.
4. **Permanent magnet:** Although neodymium-iron-boron (Nd-Fe-B) magnets were invented in 1982, they find uses only in a few applications. They suffer from some distinct disadvantages. For example, there is a marked decrease in their Curie temperature (the temperature above which a material loses its magnetism) at above 120°C temperature, and they are susceptible to corrosion. Improvement has, however been reported in their corrosion resistance through coating and plating, but with increases in costs. Potential uses of Nd-Fe-B magnets are, therefore, limited to those where the operating temperatures do not exceed 80°C (e.g., magnetic separators, magnetically levitated trains, brush-less wind power generators, MRI scanners).

5. **Rocket igniter:** In this application, 99.5% pure amorphous boron is required. The strong affinity for oxygen and the ease with which boron – particularly the amorphous type – burns, made it an eligible material for use for providing the initial ignition to fuel in rockets. But more suitable materials have now-a-days been developed.
6. **Pyrotechnics:** The characteristic green flare with which amorphous boron burns, makes it suitable for use in fire-works.
7. **Semiconductor:** The semiconductive nature of boron has opened new investigations in the field of nanotechnology. Scientists are exploring the possibility of making micro/nano-sized semiconductors by bombarding and incorporating boron atoms within micro/nano-sized diamonds.
8. **Optical fibre:** Optical fibres are used for transmitting electromagnetic energy in the form of optical energy or light waves that travel through a thinner-than-hair tube by virtue of its total internal reflection from the walls of the tube. Total reflection occurs when light passes through a medium with higher refractive index and strikes a medium with lower refractive index at a low angle. An optical fibre is made of an inner core glass tube surrounded by a cladding also made of glass which is encased in a protective outer PVC jacket. In order that total reflection can take place within the walls of the core tube, the refractive index of the cladding glass should be lower than that of the glass of the wall of the tube. One of the methods to achieve this is by adding boron to the cladding glass.
9. **Fibre-reinforced metal matrix composites:** Boron fibres are high strength, light weight materials. Such fibres are not made by wire drawing, but they actually are boron-coated tungsten or carbon filaments. The earlier practice for manufacturing boron fibre was to pass a very thin tungsten filament heated by electric current to 1000°C, through a chamber filled up with a mixture of boron, chlorine and hydrogen. After a series of reactions, a layer of boron is deposited on the tungsten filament. But since the tungsten filament remains within this boron fibre, it was somewhat heavy. To overcome this disadvantage, the tungsten filament has now been replaced by much lighter and high strength carbon filament. The manufacturing process of the carbon fibre consists in first pyrolysis of the polymers polyacrylnitril and rayon (65% C) at 200°C in presence of oxygen and then removal of the non-carbon matter by heating at 1600-2500°C. The process of coating carbon fibre with boron is the same as in case of the boron-coated tungsten filament.

Boron-fibre-reinforced aluminium is an important metal-matrix composite (MMC). This composite material containing 50% boron is light in weight (Specific gravity 2.49) and high in tensile strength. Instead of aluminium, lighter materials titanium and graphite are also used as matrices in MMCs. These MMCs are rolled into tubes and are used in cargo bays of space shuttles, in high performance sports cars, in wings and tailfins of aircrafts, etc.
10. **Plant micronutrient:** The isotope B¹¹ is believed to help movement of water and nutrients from the roots to the upper parts of plants. The exact mechanism is not known. But deficiency symptoms (weak growth and lack of health) of this element in soil show mainly in the upper parts of plants. Boron is added to some fertilizers, but scientists advocate extreme caution as even a little excess amount may be very harmful.

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SELENIUM

Selenium is an element akin to sulphur which is nonmetallic. However, some of its allotropic forms have metal-like characteristics also. It was discovered in 1817 by the Swedish chemist Berzelius. It may occur in native form associated with native sulphur, but more commonly, it is found in minute quantities as selenides of copper, lead, etc., in association with ores of copper. It also occurs in fly ash. It is usually obtained as a byproduct during refining of blister copper, in which the selenium content may be of the order of say, 0.05 per cent.

In India, recovery of selenium commenced in 1974 when 2.86 tonnes were produced. Thereafter, till early 1990s, the annual recovery generally varied between 3 and 5.5 tonnes. It reached a peak of 13.35 tonnes in 1997-98, and came down to 9.7 tonnes in 2000-01.

CRITERIA OF USE

Industrial use of selenium is centered round a few characteristics like colour, semiconducting property, peculiar light sensitivity, toughness, somewhat short range between melting and boiling points, and its chemical nature.

Selenium is pinkish red in colour, it melts at about 220°C and boils at about 685°C. Its metal-like allotropic form displays semiconductivity. But the most peculiar property is displayed by one of its allotropic forms the so called 'metallic' selenium. It exhibits photoelectric properties (i.e. it converts light energy into electrical energy) and its electrical resistance varies with the intensity of light falling on it.

USES

- (1) **Glass:** Selenium is used both as a decolourizer and as a colouring agent. Due to its pinkish red colour, it neutralizes the greenish tinge of FeSO_4 imparted to glass by iron impurities, and produces a neutral grey colour. For this purpose, just enough selenium or its compounds barium selenite and sodium selenite, can be used. On the other hand, excess selenium may be used for imparting pink or even ruby-red colour to glass. For neutralizing the colour of FeSO_4 , about 12 gm of selenium is required for a tonne of glass containing 0.15% Fe_2O_3 .

-
- (2) **Rectifier:** Rectifiers amplify and allow electric current to flow in one direction only and are used for converting alternating current to direct current. The semiconducting property of selenium makes it suitable in this application (see also chapters on Germanium and Mercury). Selenium rectifiers find use in radio and television sets, aircraft control, missiles etc.
 - (3) **Camera exposure meter:** The photoelectric property and high sensitivity of electrical resistance to changes in the intensity of incident light make selenium useful in camera exposure meters, xerox machines, facsimile machines etc. In all such applications, the light emanating from different parts of an object or a document and falling on a selenium coated plate, produces electricity which is conducted in varying degrees depending upon the intensity of light (for example, the intensity of light from the shaded or printed parts of a document is lower than that from the white parts).
 - (4) **Photocopying and offset printing:** In this case also, the photoelectric property of selenium is made use of. In a photocopier, a selenium-coated drum is charged electrically in the dark. An image of the illuminated document to be copied is then projected on it. The illuminated areas falling on the drum destroy the electric charge while the dark areas retain the charge. The drum is then dusted with a black resinous powder called *toner*, which sticks only to the charged dark areas and creates a toner image of the document. The image is transferred to paper which has the opposite charge. The heat generated in the machine fixes the toner by melting it and then setting it on the fibres of the paper, making a permanent copy. The selenium-coated plates used in offset printing also work on this principle.
 - (5) **Steel and copper:** If as little as 0.15% selenium is added during casting of stainless steel, then the product becomes fine grained and homogeneous due to the relatively short range of the liquid phase (melting point to boiling point). In forged stainless steel, and in machined copper products, addition of selenium improves the machinability due to its toughness.
 - (6) **Rubber:** Like sulphur, selenium can also be used as a vulcanizing agent, for imparting toughness and abrasion resistance. Both metal and the compound selenium dithiocarbonate can be used.
 - (7) **EnviroBrass:** Brass is an alloy of copper and zinc to which lead (3-9%) is added to improve machinability and achieve pressure tightness. This brass is used in water pipeline fittings. But recently in USA and Canada, limit of lead content in potable water has been set at 15 ppb. A new type of lead-free brasses called '*SeBiLOY*' which has later been renamed as '*EnviroBrass*', has been developed. In this alloy lead-content is limited to 0.25% and instead selenium (0.01-1.1%) and bismuth (0.5-2.2%) are incorporated. While selenium improves machinability, bismuth serves to add strength and pressure tightness.
 - (8) **Other uses:** Selenium compounds can be used:
 - (a) in paints
 - (b) as pigments for soaps, paper, ceramics, rubber, leather, etc.
 - (c) for oxidizing organic compounds
 - (d) in fungicides, insecticides etc.
 - (e) as catalysts
 - (f) as solvents for plastics
 - (g) in medicines

TELLURIUM

Tellurium owes its name to the Latin word ‘tellus’ meaning earth. This name was given by Klaproth in 1798. But tellurium was actually discovered earlier in 1789 by Kitaibel, who first isolated it from an auriferous mineral. Tellurium is closely related to selenium and sulphur and it possesses characteristics of both metals and non-metals. It is mainly recovered as a by-product from anode slime produced during refining of copper. It is also recovered as a byproduct from lead industries. In India, its annual production was only 93 kg during 2000-01, down from 621 kg in 1997-98.

Tellurium has a silvery white colour. It is fairly hard and tough. It imparts a garlic like odour to the breath of workers and this has, to some extent, deferred its extensive use as a substitute of selenium.

USES

- (1) **Glass and ceramics:** Tellurium is used as a colouring agent in art glass and ceramics.
- (2) **Rubber:** Tellurium serves as a vulcanizing agent. It imparts toughness, abrasion resistance and longer life to rubber.
- (3) **Steel casting:** Tellurium controls porosity in cast steel, and so its addition in a small quantity helps to obtain a fine-grained homogenous casting.. Tellurium is added to iron in the form of a tellurium-based alloy containing 70% Te, 25% Mn and 5% Fe to improve machinability.
- (4) **Alloy with copper:** Tellurium can be alloyed with copper. Addition of about 0.5% tellurium to copper makes the latter tough and machinable, thus facilitating mass production of certain electrical parts. This addition of tellurium affects the electrical conductivity and ductility of copper to an insignificant extent.

“Know where you are going. The great thing in the world is not knowing so much where you stand, as in what direction you are moving.”

GLOSSARY

Agglomeration: Agglomeration techniques include sintering, briquetting and pelletizing.

Alloy: An alloy is a metallic material consisting of atoms of two or more metals, or two or more elements of which most of the atoms are metal atoms. Thus, even a nonmetal can be an element in an alloy. In an alloy, the elements are admixed at the atomic level, and bulk of properties are those usually associated with metals. An alloy differs from a chemical compound inasmuch as there is no fixed formula in the former, and the contents of the elements can be varied and manipulated depending on the desirable properties to be achieved.

Atomization: Atomization is the process of dispersion of a molten metal into small particles by a rapidly moving stream of gas or liquid.

Briquette: Briquettes are made by pressing the fines with or without bonding material.

Bursting expansion: When the molten metal oxide in a furnace enters into the grains of the refractory bricks through the micro-fractures and tend to crystallize, the tremendous force of crystallization results in bursting of the bricks, and this phenomenon is known as bursting expansion.

Capacitors: Capacitors store electricity for a short period of time and ensure that the current supplied remains within narrow range of parameters – particularly in low voltage applications.

Catalysts: Catalysts increase the rate of chemical reactions without themselves undergoing permanent change.

Clay iron stone: Clay ironstone is a general term given to a ferruginous mineral occurring in the form of concretionary structures embedded in beds of clay or shale. The ferruginous mineral may be either siderite or hematite or limonite.

Coefficient of friction: It is the ratio of the friction force to the applied force. It acts perpendicular to the applied force. Higher the coefficient, more is the energy loss due to friction.

Coercive force: Coercive force is the demagnetizing force required to reduce magnetic flux density of a magnet to zero.

Corrosion: Corrosion is the degradation of a material by the environment, most people associate with rust.

Curie temperature: Curie temperature is the temperature above which a substance loses its magnetism.

Decarburization: Decarburization is the process of removal of carbon by heating in an atmosphere in which the concentration of decarburizing gases exceeds a certain value.

Diamagnetic materials: These cause the magnetic flux to move further apart, resulting in decrease in magnetic flux density compared to vacuum, the magnetic permeability of which is taken as the unit value.

Dielectric constant: It is the ratio of the capacitance of a specific sample of the material between two plates and a vacuum between the same plates. Stronger the electrical conductivity, higher is the dielectric constant. The value for air, one of the poor conductors of electricity, is 1.

Dielectric strength: Dielectric strength is a measure of the electrical insulation, and is the voltage that an insulating material can withstand before break-down. It is expressed in terms of specific resistance. The unit of measurement is volts/mm.

Dispersion: Dispersion is the rate of change of refractive index with change in wavelength of the incident light, and is expressed with reference to some wavelength.

Electrolysis: If a strong electric current is passed through a chemical compound, its decomposition into elements or parts takes place. This is called electrolysis.

Electronegative element: Atoms of some elements collect in the positive pole or anode, and those elements are called electronegative.

Electroplating: Electroplating is the process of precipitating a metal in an anodizing bath through electrolysis.

Electropositive element: Atoms of some elements collect in the negative pole or cathode, and those elements are called electropositive.

Emery: Emery is a natural mineral comprising an intimate mixture of magnetite and corundum used in powder form for polishing, smoothing and grinding purposes. On an average, emery contains Al_2O_3 65% (min), magnetite 22% (max) and SiO_2 10% (max).

Emissivity: Emissivity is a measure of the energy (heat or some other form) appearing within a substance due to absorption of incident light.

Ferrites: Ferrites are mixed oxide ceramics, which show magnetic properties similar to those of iron.

Ferrocene: First prepared in 1951, it is an organo-metallic compound of iron i.e., dicyclopentadienyl iron $[\text{Fe}(\text{C}_5\text{H}_5)_2]$.

Ferromagnetic materials: These are either naturally magnetic or attracted to a magnetic field, and may be easily magnetized. These concentrate the magnetic flux by a factor of more than 10 compared to vacuum, the magnetic permeability of which is taken as the unit value.

Hardenability: Hardenability is different from hardness, and it relates to the ease with which steels will harden and the depth of hardening obtainable.

Hard (or permanent) magnets: Once magnetized, these magnets retain their magnetic field indefinitely even after the magnetizing field is withdrawn.

International Annealed Copper Standard or IACS: This is the international standard for electrical conductivity with value of conductivity 2.8 microhm/cm^3 at 20°C .

Iron carbide: Iron carbide (Fe_3C) is reduced iron oxide with 5-6% chemically fixed carbon. It is a direct feed for steel-making.

Magnetic flux: These are the lines of force conceived as a “flow” from one pole of the magnet to the another (counterpart of current in electricity). Its unit of measurement is

gauss (or Maxwell per cm^2) which is the magnetic flux perpendicularly intersecting an area of one square centimeter.

Magnetic permeability: It is the ability to acquire magnetism in a magnetic field.

Metallization: Metallization is the reciprocal of reducibility and is expressed in terms of percentage of ore reduced to metal. Metallization also signifies the process in which very small globules of a liquid metal are blown by a spray gun and sprayed on other metal surfaces, so that the molten globules of the sprayed metal immediately solidify and interlock by flattening.

Metal matrix composites (MMC): A composite material is a materials system composed of a mixture of two or more materials deliberately combined to form heterogeneous structures with desired or intended properties. In composites, at least one of the constituents serves principally to strengthen or reinforce the composite, while another constituent, called the applications matrix, serves to confine the reinforcing constituent(s) and provides a means to distribute any applied stress. In metal matrix composites (MMCs), a metal serves as the matrix, while the reinforcing constituent can be a metal, a non-metal, an alloy or a compound.

New world: The oldest evidence of manufacture and use of iron dates back to the year 1800 BC, and this is regarded as the beginning of “iron age” and what is referred to as the “new world”.

Nitrided steel: Nitrided steel or “alloy nitride steel” or “nitralloy” is a steel which is processed so that nitrogen is absorbed by the surface which becomes intensely surface hardened, yet machinable.

Octane number: Octane number is a measure of ‘anti-knock’ value of a motor fuel i.e., the ability to resist the knock or sound produced due to its sudden and violent combustion in a spark ignition engine. For this measurement, a standard scale has been devised by assigning the value zero to heptane (C_7H_{16}) which has very poor knock resistance, and 100 to octane (C_8H_{18}) having a very high knock resistance. Octane number is the percentage of this isomer of octane in its mixture with heptane.

Old world: Right since the palaeolithic age through the neolithic age (9000-4000 BC), copper age and thereafter bronze age till 1800 BC, the entire period is referred to as “old world”.

Paramagnetic materials: These concentrate the magnetic flux by a factor of more than 1 but less than or equal to 10 compared to vacuum, the magnetic permeability of which is taken as the unit value.

Pellets: When very fine particles (size in microns) are formed into spherical objects called ‘pellets’, the process is called pelletization.

Piezoelectricity or electrostriction: Piezoelectric crystals can change alternating mechanical strains into electrical impulses and vice versa.

Polarization: Polarization is the process by which hydrogen gas liberated in a chemical reaction goes towards carbon anode and accumulates around it.

Positive temperature coefficient of resistivity or PTC: It is increase in resistivity with increase in temperature.

Powder metallurgy: Powder metallurgy is the process whereby many small components are produced by fabricating metal powders or metal and ceramic powders together.

Radioactivity: Radioactivity is the spontaneous disintegration of certain heavy elements accompanied by the emission of high energy radiation, which consists of three kinds of rays: 'alpha particles', 'beta particles' and 'gamma rays'.

Reducibility: Reducibility is a measure of acceleration in the reduction process with increase in temperature in a scale of 0-1.

Refractory: Refractory materials are defined as those resistant to heat and having a melting temperature of not less than 1580°C. The function of refractory lining is not only to withstand high temperature, but also to resist temperature fluctuation, slag and metal penetration, abrasion, and erosion by hot gases and molten slags and metals.

Semiconductor: These are materials with resistivity intermediate between metals (resistivity $< 10^4$ ohms/cm) and insulators (resistivity $> 10^3$ ohms/cm).

Sinter: By application of just enough heat to fuse the corners of ore particles, they are made to join together to form a lumpy mass. This product is called 'sinter'.

Soft magnets: These can be magnetized easily, for example by electric current travelling in an electric coil wrapped around a soft magnetic core, but they lose their magnetism once the current is turned off.

Taconite: Taconite is the name given to fine-grained compact siliceous iron formations – ferruginous chert or ferruginous slate — containing very finely disseminated oxides of iron, less than 20 mesh in size.

Welding: Welding is a metal-joining process wherein coalescence is produced by heating to suitable temperature with or without pressure and with or without the use of filler metal".

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