Handbook of Flotation Reagents: Chemistry, Theory and Practice

Flotation of Industrial Minerals

Volume 3

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Introduction

In the past several decades considerable emphasis was placed on investigation of flotation properties of industrial minerals. The interest in process development for beneficiation of various industrial minerals also comes from the growing need to recover economic minerals from lower grade ores. In general terms these ores in which the minerals exist as ores are associated with, complex, silicates do not respond to the concentration methods used to treat higher-grade less complex mineral silicate ores.

The literature on beneficiation of silicate-containing ore is highly fragmented, and have been published in a number of journals and books between the 1980s and 1990s.

This volume of the book is devoted to the beneficiation of most important industrial minerals. The book contains details of fundamental research work carried out by a number of research organizations over several decades. For more industrial minerals included in this book, plant practices are presented.

The objective is to provide the practical mineral processor, faced with the problem of beneficiation of difficult-to-treat ores, with a comprehensive digest of information available. Thus enabling him to carry out his test work in a more systematic manner and to assist in controlling operating plants.

The book will also provide valuable background information for research workers, university students, and professors. The book will also provide comprehensive references of world literature on the subject.

A new technology for a number of industrial minerals developed by the author is also contained in Volume 3 of the book.

CHAPTER

Flotation of Phosphate Ore

26

CHAPTER OUTLINE

26.1 Introduction

The upgrading of phosphate ores using froth flotation method has been practiced for at least 65 years. Extensive research work has been carried out in the last 25 years, on various phosphate-containing ores. Despite of extensive research and industrial experience, there are some challenges remaining in particular in beneficiation of siliceous, calcite, and heavy mineral containing phosphate ores.

The upgrading of phosphate ores by some form of froth flotation has been practiced in the last 60 years. A number of useful references exist which summarize the history and the associated chemical reagents technology base. Industrial processed phosphate ores are generally classified into two major types: marine sediments from southeastern United States and igneous ores from South Africa, Russia, Finland, and Brazil. The major minerals comprising these ores are apatite, primarily calcium phosphate, silica and clay, with some complex deposits containing dolomite and calcite. Each of these geographic areas has developed their own unique processing technology for beneficiation of these ores. This chapter summarizes the beneficiation technology of various ore types and describes the most important type of research and development on various ore types.

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26.2 Phosphate deposits and its origin

There are two main types of phosphate ore deposits. These are (1) igneous, alkaline complexes and carbonatites and (2) marine sedimentary deposits. There are other more complex deposits containing phosphate and titanium. Other less important sources are by-product apatites from iron ore processing. The principal phosphate mineral is apatite, which has a general formula $Ca_3X(PO_4)_3$. The X may be chlorine, fluorine, or hydroxyl ion. Fluoro- and hydroxyapatite are most common.

Uranium is present in most sedimentary phosphate deposits in the concentration of about 100 ppm and is extracted as a by-product during phosphoric acid production.

Igneous deposits. Igneous carbonatite deposits account for about 15% of the world phosphate production and their processing is relatively simple. In these ores, apatite is well crystallized with a nonporous surface, which gives it better flotation properties than amorphous form associated with sedimentary deposits. There are a number of large deposits that treat igneous ore types.

Sedimentary deposits. These deposits account for about 70% of phosphate production. The phosphate typically occurs as nodules or phosphatic debris up to 15 or 20 mm in size. The gangue is clay carbonates and silicates. Salt is also a frequent contaminant. Processing of this ore type largely depends upon the type of gangue present in the ore.

Complex—iron titanium phosphate ores. These are of granite gneiss origin and may also contain pyroxenite. Some of the ore types may contain pyrochlore minerals. Beneficiation of these ore types involves a relatively complex reagent scheme and flow sheet.

In general the phosphate minerals vary in composition depending on the type of ore. Table 26.1 shows the phosphate minerals usually found in commercial ore bodies.

It should be noted that many different substitutions are found in phosphate minerals. Silica and alumina may occur in place of some of the phosphate, and calcium may be replaced in part by rare earth lanthanide.

26.3 Flotation beneficiation of different phosphate ore types

26.3.1 Carbonatite and dolomitic ores with and without the presence of silicate

The separation of apatite from calcite is considered difficult as both minerals contain some cation in its lattice and therefore they have similar flotation properties. It has

Table 26.1 Phosphate Minerals Usually Found in Commercial Ore Bodies

Mineral	Formula
Dahllite	$Ca_{10}\ (PO_4)_6-(CO_3)x(O,HF)_2+x$
Fluorapatite	$Ca_{10}\ (PO_4)_6\ (FOH)_2$
Francolite	$Ca_{10}\ (PO_4)_6-x\ (CO_3)\ x\ (F,OH)_2+x$
Hydroxyapatite	$Ca_{10}\ (PO_4)_6-x\ (CO_3)\ x\ (OH)_2+x$

been found that flotation behavior of these two minerals using either anionic or cationic collector is virtually the same.

A number of researchers [1,2] have developed methods for beneficiation of calcareous phosphate ores using the fatty acid method.

Studies also performed using sodium oleate as the selective collector for apatite [3]. Using sodium oleate–sodium silicate system, the selectivity is affected by flotation pH and the level of sodium silicate.

Figure 26.1 shows the effect on pH on apatite and calcite using sodium oleate–silicate system.

The highest apatite recovery was achieved between pH 8.0 and pH 9.0. Experimental testwork was also performed at pH 8.0 with different levels of sodium silicate. These results are presented in Figure 26.2. It appears from the results that higher levels of sodium silicate have no significant effect on apatite and calcite grade recovery.

Most recently, a number of processes are developed for sedimentary carbonate–apatite flotation using inverse flotation of carbonates with fatty acid collector and depression of apatite using various depressant.

Some of the processes developed by various research organizations are discussed below.

Sulfuric acid depression system [4]. In this process, the apatite minerals are depressed by using sulfuric acid in slightly acid pulp (pH = 5.0–5.5), while floating carbonate using fatty acid. It is interesting to note that due to rapid pH increase in the presence of calcite, the conditioning time with H_2SO_4 and collector was only 1 min.

The results of this study showed that this process is relatively selective and good concentrate grade can be produced.

Aluminum sulfate/Na, K-tartrate process [5]. The process uses Na, K-tartrate and aluminum or iron sulfate to depress apatite and oleic acid with pine oil to float carbonate gangue at pH 7.5–8.2. It was postulated that conditioning of the pulp with

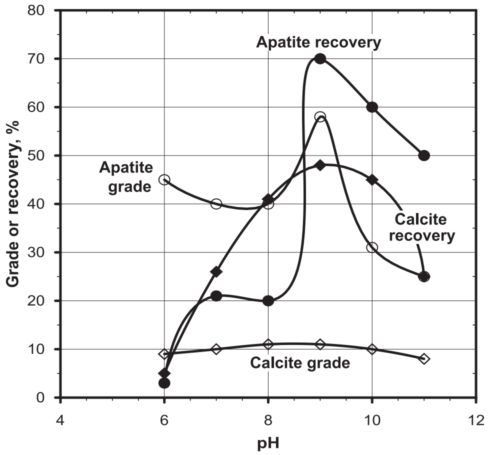

FIGURE 26.1

Flotation results as a function of pH (sodium oleate = 200g/t, sodium silicate = 250g/t).

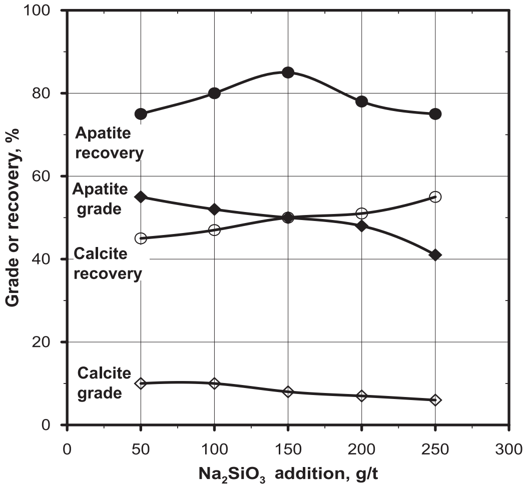

FIGURE 26.2

Effect of level of sodium silicate on calcite apatite separation at pH 8.0.

$Al_2(SO_4)_3$ plus K-tartrate mixture (Ratio 1:2) causes the formation of a strongly electronegative film on the phosphate surface that may hinder the adsorption of anionic collector which causes apatite depression. Using this method an apatite concentrate assaying 27.1–30.7% P_2O_5, 42.9–55% CaO, and 1.5–6.3 MgO was obtained at 66–84.7% P_2O_5 recovery was obtained. The MgO content of concentrate was higher than acceptable.

US bureau of mine process [6]. Using this process the phosphate minerals are depressed by hydrofluorosilicic acid (H_2SiF_6), while carbonate minerals are floated using fatty acid emulsions. This process has been used to float dolomite in a pilot plant scale from an Idaho phosphate ore. Distilled tall oil was used as a collector (1–2 kg/t) at pH 6.0. This process gave relatively poor selectivity. The best phosphate concentrate grade assaying 25–33% P_2O_5 and 1.4–6.5% MgO.

Tennessee valley diphosphonic acid process [7]. In this process, phosphate minerals are depressed using ethylidene hydroxydiphosphonic acid while carbonate is floated using a fatty acid collector at pH 6.0–6.5. Using this method, phosphate concentrate assaying 29–32% P_2O_5 and 1.4–4.7 MgO was obtained at P_2O_5 recovery of 71–83% P_2O_5. The MgO/P_2O_5 weight ratio was too high.

Industrial minerals and chemical corporation cationic process [8]. This process is best applied on the ores with low silica content or feed from which silica is first removed by using bulk phosphate calcite flotation and depression. Carbonate minerals (calcite and dolomite) are depressed by hydrofluoric acid in slightly acid pH (5.0–6.0) while floating phosphate with amine (Armac T, tallow amine acetate) and fuel oil.

Flotation test results have indicated that MgO content of the concentrate was too high (1.8–4.2% MgO). The P_2O_5 recovery using this process was relatively low.

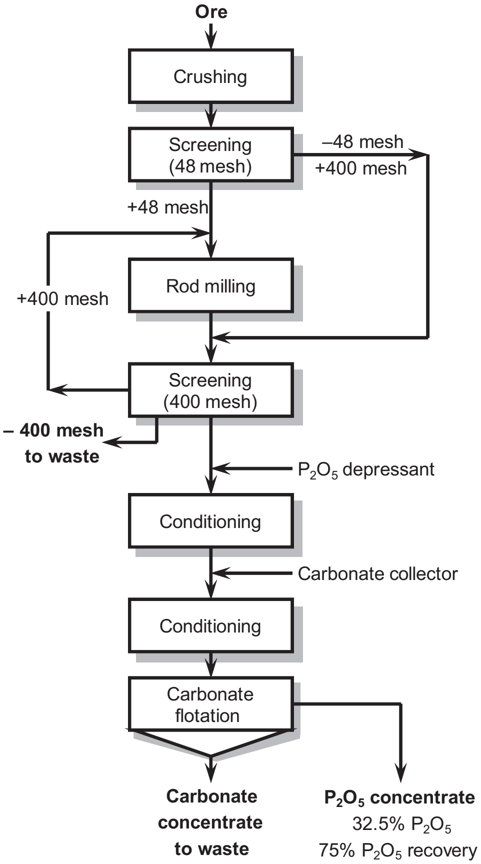

FIGURE 26.3

Flow sheet used in beneficiation of carbonatite ore without silicate present in the ore.

Phosphoric acid process [9]. In this process, phosphoric acid is used to depress phosphate minerals in slightly acid pH (5.0–5.5) while floating carbonate with fatty acid. It is postulated that phosphate ions are specifically adsorbed on the phosphate surface causing formation of electronegative film thus causing phosphate depression. In this study oleic acid was used. Flotation test results showed that the concentrate averaged 1.0 MgO giving the ratio of MgO/P_2O_5 of 0.03, which is acceptable. Using this method, good P_2O_5 grade and recovery was achieved.

Using the above process, two flow sheets were used; these include:

1. Direct carbonate flotation. This flow sheet (Figure 26.3) is used when the ore contained small quantities or no silicate.
2. Bulk, carbonate phosphate flotation followed by carbonate/phosphate separation. This flow sheet (Figure 26.4) is used on the ore that contained silicate together with carbonate.

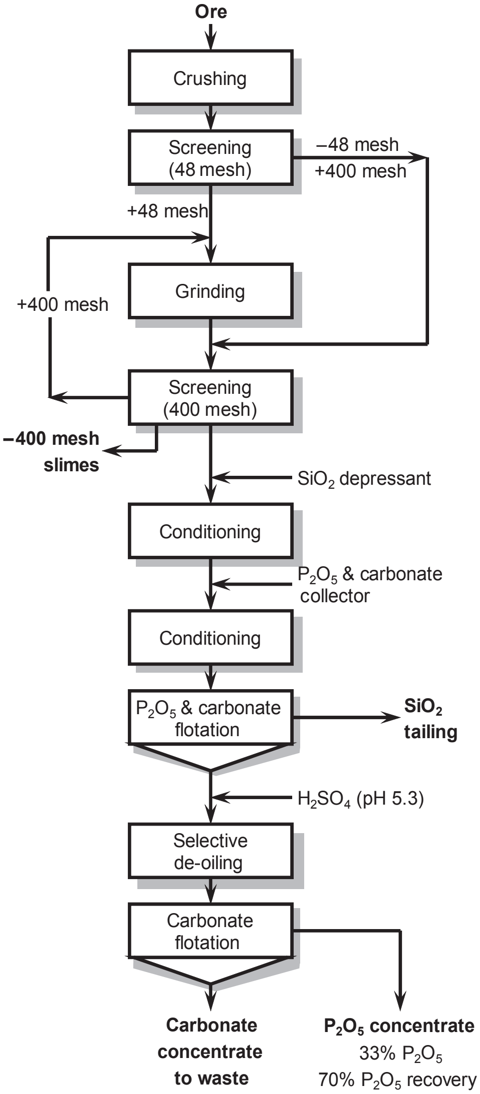

FIGURE 26.4

Two-stage carbonate phosphate flotation flow sheet.

The metallurgical results using some of the above described process are shown in Table 26.2.

Good metallurgical results were achieved using H_2SO_4, $Na_5P_3O_{10}$, and H_2PO_4. Other depressants gave poor selectivity and poor metallurgical results. It should be noted that fineness of grind presence of fine slime and type of ore body plays an important role in separation efficiency. Usually good metallurgical results are obtained at coarser grind and low slime content.

Table 26.2 Metallurgical Results Obtained Using Various Reagent Combinations.

Test Conditions	Product	Wt %	Assays %		% Distributed		Separation Efficiency
			P_2O_5	MgO	P_2O_5	MgO	
Oleic acid = 2 kg/t H_2SO_4 = 0.8 kg/t pH = 4.0	P_2O_5 concentrate	39.8	38.5	0.8	82.1	3.1	79
	Dolomite (froth)	60.2	5.5	16.6	17.9	96.9	
	Head	100.0	18.5	10.3	100.0	100.0	
$Na_5P_3O_{10}$ = 0.75 kg/t Oleic acid = 0.75 kg/t pH = 5.5	P_2O_5 concentrate	32.7	36.6	0.8	73.3	2.3	71
	Dolomite (froth)	67.3	6.5	13.4	26.7	97.7	
	Head	100.0	16.3	11.3	100.0	100.0	
H_2PO_4 = 3.0 kg/t Oleic acid = 1.5 kg/t pH = 5.0	P_2O_5 concentrate	35.7	36.1	1.0	79.4	3.1	76
	Dolomite (froth)	64.3	5.2	17.5	20.6	96.9	
	Head	100.0	16.3	11.6	100.0	100.0	
Diphosphonic acid = 0.5 kg/t Tall oil = 2.0 kg/t pH = 5.0	P_2O_5 concentrate	34.6	33.4	2.1	70.0	6.4	63
	Dolomite (froth)	65.4	7.6	16.2	30.0	93.6	
	Head	100.0	16.5	11.3	100.0	100.0	
Armac T = 0.1 kg/t HF = 0.36 kg/t pH = 5.0	P_2O_5 concentrate	25.4	33.3	2.3	49.7	5.3	44
	Dolomite (froth)	74.6	11.5	14.2	50.3	94.7	
	Head	100.0	17.0	11.2	100.0	100.0	
Oleic acid = 1.5 kg/t $(Al_2SO_4)_3$ = 0.3 kg/t Tartrate = 0.6 kg/t pH = 7.8	P_2O_5 concentrate	21.4	29.0	5.9	36.8	11.1	26
	Dolomite (froth)	78.6	13.5	12.9	63.2	88.9	
	Head	100.0	16.9	11.4	100.0	100.0	
Tall oil = 1 kg/t H_2SiF_6 = 2 kg/t pH = 6.0	P_2O_5 concentrate	34.5	25.9	6.8	53.0	20.6	32
	Dolomite froth	65.5	12.1	13.7	47.0	79.4	
	Head	100.0	16.9	11.3	100.0	100.0	

26.3.2 Direct flotation of phosphate from the ores containing carbonate and dolomite

In recent studies, research work was carried out on direct apatite flotation from carbonaceous gangue minerals using various depressant and or new collectors.

A new process for the separation of a phosphate mineral from carbonaceous gangue using direct apatite flotation has been developed [10]. The process is based on carbonaceous gangue depression using phenol–formaldehyde copolymers such as Resol, novolak, and melamine-modified novolak. Novolak can be prepared from phenol and formaldehyde, in the presence of acid catalyst. Resol on the other hand may be prepared from phenol and formaldehyde in the presence of alkali catalyst.

These depressants are tested on the ore assaying 6.9% P_2O_5, 30.8% carbonates and the remaining being silicates.

The results obtained with different dosages of collector and depressants are shown in Table 26.3. Collectors used in these experiments were tall oil fatty acid modified with triethoxy butane.

Another depressant system consisting of Depressant System A3-2 plus oxalic acid was examined on the ore from Lalitpur, Uttar Pradesh, India [11]. The ore assayed 15% P_2O_5, 52% SiO_2, 3% Al_2O_3, 28% CaO. Collector used in the experimental testwork (Emulsion A) was a mixture of tall oil (45%) plus sarcosine OS100 (45%) modified with coal oil (10%). Lilaflot OS100 is manufactured by AKZO Nobel.

Depressant A3-2 is a mixture of sodium silicate aluminum sulfate and sodium bisulfate in a ratio of Na_2SiO_3:$Al(SO_4)_3$:$Na_2S_2O_3$ = (38:38:24).

The use of oxalic acid improved silica rejection. The effect of oxalic acid additions on silica assays of the apatite concentrate is illustrated in Figure 26.5.

Collector emulsion A1 is a highly selective collector for the ores containing silica, calcite, and dolomite. The effectiveness of this collector is compared with other collectors in Figure 26.6.

Continuous test results obtained on the ore are shown in Table 26.4.

The other known method is calcination of the ore at about 700 °C followed by quenching, washing, and apatite flotation. No industrial application of this method exists.

Table 26.3 Effect of Phenol–Formaldehyde Copolymers on Phosphate Flotation

Collector, g/t	Frother, g/t	Depressant, g/t	Apatite Concentrate % P_2O_5	Apatite Concentrate Recovery %
50	10	Resol = 125	35.9	80.6
100	10	Resol = 250	28.7	78.3
100	10	Resol = 350	35.8	81.3
250	10	Resol = 200	35.1	84.9
250	10	No depressant	18.4	63.7
250	10	Novolak = 50	30.2	93.9

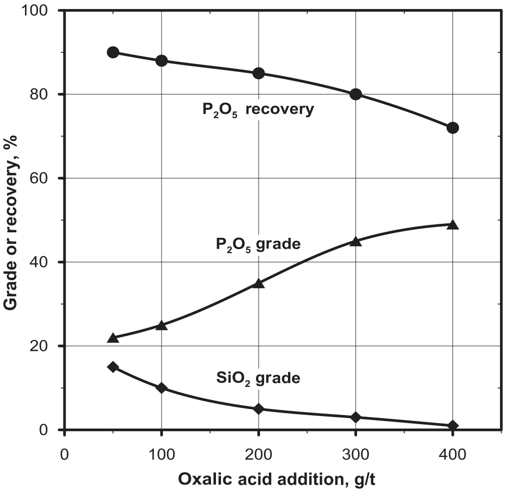

FIGURE 26.5

Effect of oxalic acid level on silica rejection during apatite flotation.

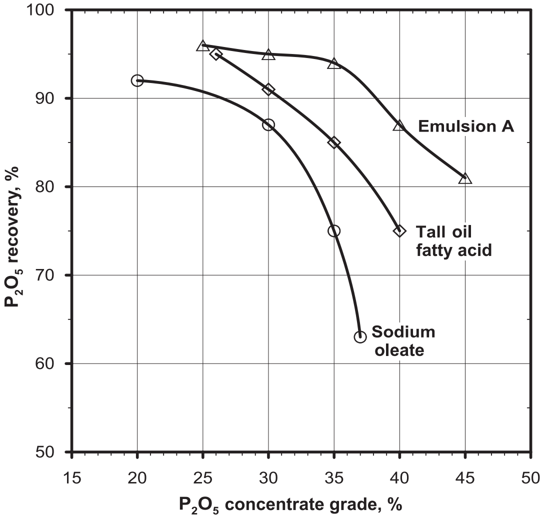

FIGURE 26.6

Effect of collector type on phosphate grade recovery relationship.

26.4 Beneficiation of high iron and mixed iron, titanium ores

A number of the phosphate ores of sedimentary or igneous origin have high iron contents, which represent a problem in beneficiation of phosphate. Some ore also contains significant quantities of ilmenite.

Table 26.4 Results of Continuous Locked Cycle Test Using New Depressant and Collector System

Reagents Added, g/t	Product	Wt %	Assays %				% Distribution
			P_2O_5	MgO	SiO_2	Fe_2O_3	P_2O_5
Depress A3.2 = 900 Oxalic acid = 200 Coll EmA[a] = 500	P_2O_5 Cl. concentrate	42.40	36.22	0.08	5.50	0.80	97.5
	P_2O_5 combined tails	57.60	0.68	–	–	–	2.5
	Feed	100.00	15.75	–	–	–	100.0

[a] *Collector EmA- modified fatty acid with Fuel oil and Pine oil.*

Table 26.5 Effect of Modulus of Sodium Silicate on Flotation Performance of High Iron Apatite Ore

Modulus of Sodium Silicate	Grade at 90% P_2O_5 Recovery			Ratio P_2O_5
	% P_2O_5	% Fe_2O_3	% Al_2O_3	$Fe_2O_3 + Al_2O_3$
1.0	36.2	7.1	0.28	4.9
2.1	37.5	6.0	0.25	6.0
3.3	35.8	8.4	0.31	4.1

Various processes have been developed for the removal of iron from apatite concentrate including scrubbing for surface cleaning, gravity separation, magnetic separation, and flotation using specific iron containing gangue depressants. Often, a combination of two or more of these processes is used to reduce iron content of the apatite concentrate to acceptable levels.

Attrition scrubbing is used to remove iron coating from the apatite mineral surfaces, which is often the case with crystalline apatite contained in igneous ore.

Heavy liquid separation of iron bearing minerals is also practiced. Good separation can be achieved with coarsely liberated particles.

One of the methods studied involves the use of silicates with a different modulus [12]. The results indicate (Table 26.5) that the silicate with a modulus of 2, improved iron rejection during phosphate flotation.

Experiments conducted with different mixture of silicate and metal salt showed improvements in apatite grade and iron rejection. Table 26.6 shows the effect of different ratios of silicate and metal salt on apatite grade and recovery. In these experiments $AlCl_3$ and $CaCl_2$ were used.

In beneficiation of high iron ores a typical reagent scheme includes sodium silicate, caustic tapioca, or corn starch as iron and silicate depressants and tall oil fatty acid/fuel oil mixture for apatite flotation (Figure 26.7).

Most recently extensive laboratory and pilot plant studies were conducted on complex igneous ore containing iron, ilmenite and apatite [13] from Canada.

Table 26.6 Effect of Different Silicate–Metal Salt Mixtures on Apatite Flotation from High Iron Ore

Metal Salt	Metal/ Silica Ratio	Assays %			% Distribution		
		P_2O_5	Fe_2O_3	Al_2O_3	P_2O_5	Fe_2O_3	Al_2O_3
$AlCl_3$	0.2	36.5	6.6	0.25	85.6	9.1	24.9
$AlCl_3$	0.4	37.8	4.7	0.23	83.6	6.1	21.6
$AlCl_3$	0.6	37.1	4.6	0.24	79.7	5.8	21.9
$CaCl_2$	0.2	38.2	5.5	0.23	83.5	7.0	21.4
$CaCl_2$	0.4	38.5	4.4	0.23	82.5	5.5	21.0
$CaCl_2$	0.6	38.3	4.7	0.22	76.4	5.5	18.7
No salt	–	36.2	7.9	0.30	86.5	11.1	27.4

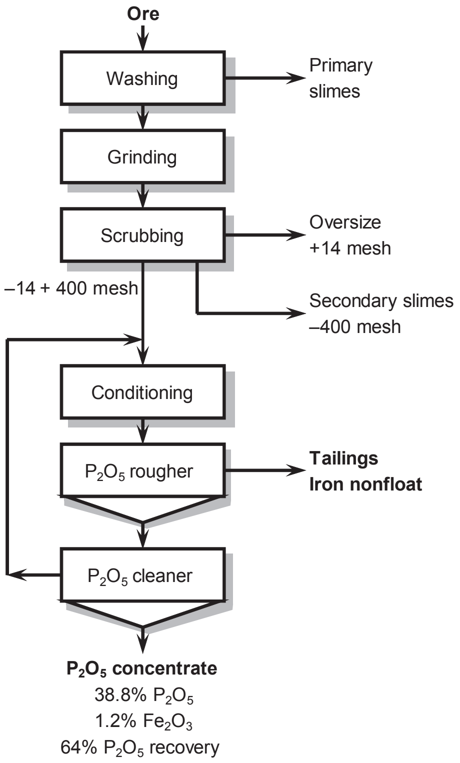

FIGURE 26.7

Flow sheet used in flotation of apatite from the ore that contain high iron.

The process developed involved grinding magnetic separation followed by direct apatite flotation.

The final reagent scheme that has been confirmed in the pilot plant operation is shown in Table 26.7.

Depressant A4 is composed of lignin sulfonate (30% sodium silicate (50) and $CaCl_3$ (10%)).

Metallurgical results obtained in the pilot plant are shown in Table 26.8. Excellent concentrate grade and apatite recovery were achieved using the reagent scheme shown in Table 26.7. The flow sheet used (Figure 26.8) a double open circuit cleaning, which resulted in improvement in the metallurgical results.

Two major factors played a significant role in achieving satisfactory apatite metallurgical results. These are:

- Double open circuit cleaning where low recirculating load of gangue was possible to maintain resulted in a stable circuit. In close circuit cleaning the silica

Table 26.7 Reagent Scheme with Point of Reagent Additions Developed for Beneficiation of Apatite Ore that contain High Iron/Ilmenite

	Additions, g/t		
Reagent	**Condition**	**Rougher**	**Cleaning**
Depressant and Modifier			
Caustic tapioca starch	500		400
Depressant A4	300		200
Na_2CO_3	800		600
Collector			
Causticized tall oil	500	100	200

Table 26.8 Apatite Metallurgical Results Obtained in a Continuous Pilot Plant Test

		Assays %				**% Distribution**			
Product	**Wt %**	**P_2O_5**	**TiO_2**	**SiO_2**	**Fe_2O_3**	**P_2O_5**	**TiO_2**	**SiO_2**	**Fe_2O_3**
P_2O_5 Cl. concentrate	16.56	40.0	0.13	0.68	0.80	87.6	0.2	0.6	0.4
P_2O_5 com. tails	61.07	1.09	11.3	32.48	27.7	8.8	69.3	97.5	48.9
Middlings	0.70	31.25	2.29	5.92	6.6	2.9	0.2	0.2	0.1
Magnetics	21.67	0.24	13.92	1.59	80.6	0.7	30.3	1.7	50.6
Feed	100.0	7.57	9.95	20.34	34.5	100.0	100.0	100.0	100.0

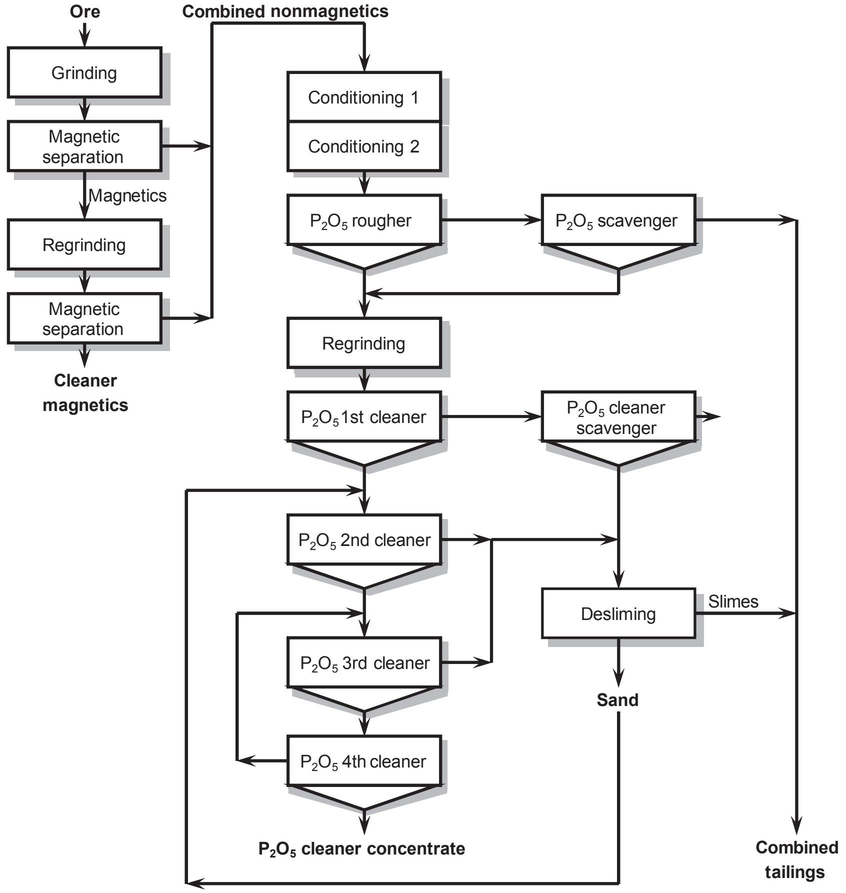

FIGURE 26.8

Flow sheet developed for beneficiation of mixed apatite-iron and ilmenite ore.

assays of the apatite concentrate was 11.2% SiO_2 resulting in a low apatite concentrate grade of 33% P_2O_5.

- The use of causticized tall oil resulted in significant improvement in selectivity. The effect of different collectors on apatite grade recovery relationship is illustrated in Figure 26.9.

26.5 Plant practice in beneficiation of phosphate ores

There are many operating plants around the world treating different ore types, which are described in this chapter. One of the basics is the use of fatty acid as a main collector for most of the operating plants. Modifiers and depressant system may vary

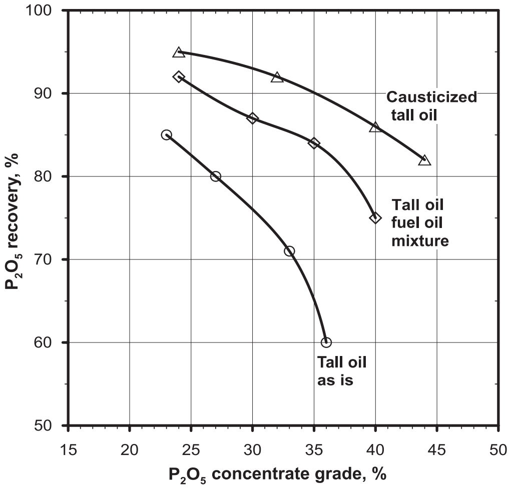

FIGURE 26.9

Effect of different modifications of fatty acid on apatite grade recovery relationship.

from plant to plant. The flow sheet configuration also depends on the type of ore treated. In this section, a number of operating plants that treat different ore types are presented.

26.5.1 Florida phosphate treatment plants

The phosphate mining and beneficiation have been carried out by about 15 different mining companies with about 25 operating plants. The total production of phosphate pebbles and flotation concentrate accounts for about 75% of the total US production. Most of the operating plants have similar flow sheets except three plants where plus 14 mesh pebbles are ground followed by amine flotation of silica.

A general Florida phosphate flow sheet is presented in Figure 26.10.

There is, however variation in treatment of coarse fraction from 14 to 20 mesh. In phosphate and silica flotation a variety of collectors are used. Table 26.9 shows reagents used in various plants for treatment of phosphate from Florida.

Most of the losses of phosphate during treatment of Florida ores occur in minus 150 mesh slime fraction. The final concentrate grade in most of the plants averaged 33–34% P_2O_5 but overall recovery varies from plant to plant.

26.5.2 Vernal phosphate rock mill

The Vernal Mill is located in Utah, USA. The mill treats sedimentary rock from the phosphoria formation. The ore minerals identified are collophane, dahllite, and francolite, all being carbonate–apatite minerals with chemical formula $Ca_5(PO_4CO_3OH_3)$ (FOH). Collophane is most abundant and is liberated at about 100 mesh size. The

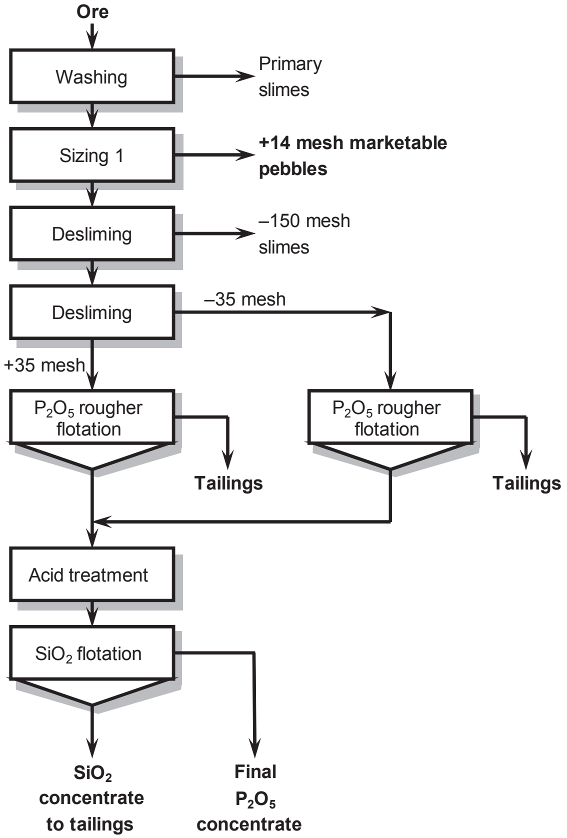

FIGURE 26.10

General flow sheet for beneficiation of Florida phosphates.

Table 26.9 List of Collectors Used in Beneficiation of Florida Phosphate

Phosphate Circuit			**Silica Circuit**
Collectors	**Extenders**	**Modifiers**	**Collectors**
Soap skimming's	No. 5 fuel oil	NaOH	Liquid amine blend
Tall oil heads	No. 6 and No. 5	Antidous	Liquid tallow amine blend
Tall oil blend	Fuel oil	NH_3	Condensate type amine

ore treated uses split circuit flow sheet, which included primary phosphate rougher and cleaning followed by regrinding or rougher tailing and P_2O_5 scavenging. The scavenger concentrate contains dolomite, which is removed by reverse flotation. The plant flow sheet is presented in Figure 26.11.

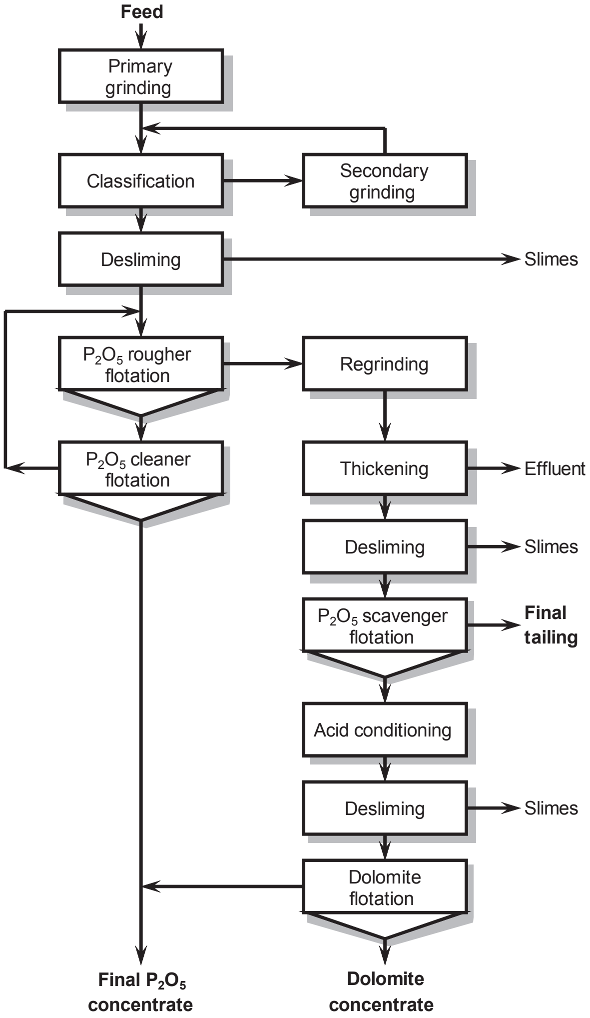

FIGURE 26.11

Vernal plant flow sheet.

The reagent scheme used in the Vernal plant in the various phosphate and carbonate circuit are presented in Table 26.10. The primary rougher is conditioned at 70% solids for about 10 min with additions of reagents. Scavenger feed is conditioned at pH 7.9 in the presence of reagents followed by scavenger flotation.

Carbonate flotation is performed in slightly acid pH of 5.6.

The final concentrate grade assaying 31% P_2O_5, 0.59% MgO, and 0.55% soluble Fe_2O_5 was achieved at about 78% overall P_2O_5 recovery.

Table 26.10 Reagent Scheme Used in Vernal Plant

Reagent Additions, g/t			pH	
P_2O_5 Rougher	**P_2O_5 Scavenger**	**Carbonate Ore**	**P_2O_5**	**Carbonate**
Parmak fatty acid = 800	Parmak fatty acid = 600	Stepan B160 = 300	8.0	5.6
Stepan B120 = 200	Stepan B120 = 200	Frother = 30		
Diesel fuel #2 = 400	Diesel fuel #2 = 150			
9743 Frother = 50	9743 Frother = 50			

Stepan B120 is petroleum sulfonate.

26.5.3 Serrana operation, Brazil

Serrana operation is located in Jacupiranga province south of Sao Paolo. The low-grade carbonatite ore averaged 5% P_2O_5, 70% calcite, 10% dolomite, 5% magnetite, and minor amounts of mica. The concentrating plant uses direct apatite flotation method while, calcite acid dolomite is depressed. The actual plant flow sheet is shown in Figure 26.12. Over the years a number of modifications were made in the grinding circuit with the objective of reducing apatite losses in the slime fraction.

The basic reagent scheme includes NaOH for pH control. Modified starch and sarcosine collector type concentrate grade assaying 35.5% P_2O_5 at 74% P_2O_5 recovery.

26.5.4 Other operating plants

There are about 35 other operating plants that treat phosphate ores. There are three general flow sheets used in these plants; these are:

- Direct phosphate flotation. These plants utilize fatty acid collector and various gangue depressants such as silica, starches, and dextrius.
- Phosphate flotation followed by reverse silica flotation.

In these plants phosphate is floated using various tall oils fatty acids, in the presence of depressants, followed by apatite depression and silica flotation using amine collector at slightly acid pH.

- Apatite/dolomite/calcite bulk flotation, followed by apatite depression and dolomite/calcite flotation. These plants are utilized in fatty acid in both bulk and dolomite calcite circuits.

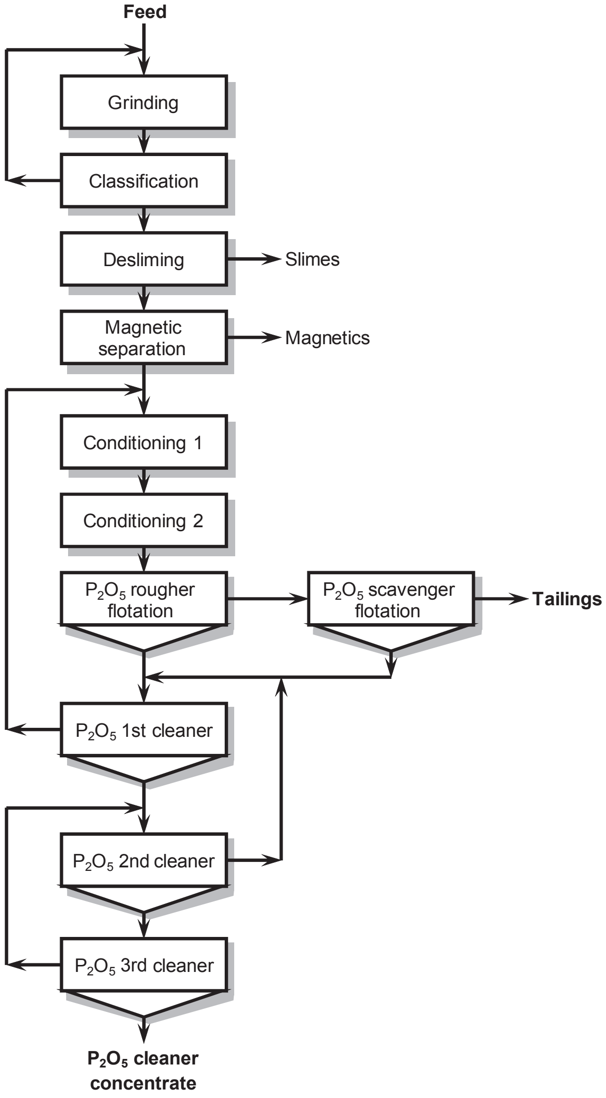

FIGURE 26.12

Generalized flow sheet used in Serrana plant.

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CHAPTER

Beneficiation of Beryllium Ores

27

CHAPTER OUTLINE

27.1 Introduction

Most of beryllium production comes from beryl and therefore flotation properties of beryl are examined in detail by various research organizations. Because beryl is found in the form of large crystals in various ore types, recovery of beryl from these ores is accomplished by sorting and or selective grinding due to the fact that the hardness of beryl is 7.5–8 (Mohs scale); during grinding, most of the gangue is ground finer than beryl and beryl is left in the coarse fraction, which is recovered by screening.

From the fine grained ore, beryl is recovered using the flotation method, where either anionic or cationic flotation is used.

Very little is known about flotation of other beryllium minerals such as phenacite and bertrandite. Research work carried out by some research organizations [1,2] on complex phenacite-containing ores have shown that phenacite can be readily floated using modified fatty acid. Using this method a concentrate grade assaying 40% BeO_2 at 85% recovery was achieved.

27.2 Ore and minerals of beryllium

In nature, about 30 beryllium minerals are known of which six to eight have economic value. The main beryllium minerals are presented in Table 27.1.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00002-6

Table 27.1 Beryl Minerals of Economic Value

Mineral	Chemical Formula	BeO_2 Content %	Specific Gravity, g/cm^3	Hardness MoOS Scale	Color
Beryl	$Al_2\ Be_3\ (Si_6O_{18})$	11–14.3	2.6–2.9	7.5–8	White, colorless greenish
Xrizoberyl	Al_2BeO_4	19.8	3.5–3.8	8.5	Yellow, yellow-blue, bluish
Phenacite	$BeO_2(SiO_4)$	45.5	3.0	7.5	Colorless, brown yellowish
Gelvin	$Mn_8(BeSiO_4)_6.S_2$	11–14.2	3.3	6–6.6	Yellow, brown, green
Getgelvin	$Zn_8(BSiO_4)_6.S_2$	11–14	3.66	–	Reddish
Danolit	$Fe_8(BeSiO_4).S_2$	12.7–14.7	3.40	5.5–6	Yellow, green
Bertrandite	$Be_4(Si_2O_7)(OH)_2$	39.6–42.6	2.6	6	White, colorless, yellowish
Evklaz	$Be_2Al_2Si_2O(OH)_2$	–	3.1	7.5	Greenish

Beryl is the most abundant in the other beryllium minerals and is mostly found as crystalline structures in several forms which include:

1. Izumrud contains inclusions of chromium, which gives a bright green color.
2. Aquamarine contains inclusions of two valent iron and has a greenish color.
3. Rosterite is a colorless beryl form. It is known as alkaline beryl (about 0.5% alkalinity).

Xrizoberyl: It is known as a gem mineral which comes from its bright green color. Usually xrizoberyl (11) contains: Up to 6% Fe_2O_3, 3% TiO_2, and 0.4% Cr_2O_3. These inclusions dictate the color of xrizoberyl.

Phenacite: It usually contains MgO, CaO, Al_2O_3, and Na_2O and an association often is found in pegmatites in association with beryl, xrizoberyl, topaz, quartz, mica, and hornblende. The color of phenacite is unstable and depends on the association with other minerals.

Gelvin is sometimes paramagnetic and often contains manganese and iron or zinc. It is soluble in hydrochloric acid. It has a yellowish color. Gelvin is usually found in pegmatite lenses in association with quartz and albite. In skarn deposits are associated with magnetite and fluorite.

Bertrandite is usually found in pegmatite lenses in association with beryl, tourmaline, muscovite, and albite. In some deposits in USA, it is often found with beryl and fenekite.

Beryllium deposits: The main types of beryllium containing deposits include pegmatites and hydrothermal-pneumatolytic deposits which can be divided into several subgroups depending on the types of beryl ores and also the types of other minerals

Table 27.2 Industrial Types of Beryllium Deposits

Deposit Type	Ore Types and Their Industrial Value	Beryl Minerals	Associated Minerals
Block pegmatites muscovite-albite	Ore with muscovite, quartz mica with fine crystalline beryl	Beryl	Columbite, tantalite
Mixed pegmatites muscovite-albite	Ore with muscovite, quartz mica with fine crystalline beryl	Alkaline beryl	Columbite, tantalite
Mixed spodumene lepidolite-albite pegmatites	Spodumen-quartz albite ore with fine crystalline beryl. This ore type gave about 90% of all beryllium production	Alkaline beryl	Spodumene, columbite, tantalite, cassiterite, lepidolite
Intermixed pegmatites and pneumatolites	Mica plagioclas and silica plagioclas lenses with beryllium; important but not abundant	Beryl (izumrud) xrizoberyl, phenacite	–
Hydrothermal-Pneumatolytic			
Alumosilicates beryl containing altered granites	Muscovite-quartz ores with beryl; a potential industrial deposits	Beryl	Wolframite
Beryl containing quartz-muscovite-topaz lenses	High-temperature formations of quartz lenses; important industrial deposits	Beryl (gelvin, bertrandite)	Wolframite, cassiterite, molybdenite
In carbonatite matrix beryl containing skarns	Magnetite fluoride ores with xrizoberyl and gelvin –danalite; potentially important deposits	Xrizoberyl, gelvin, danalite, fenakite	Shelite
Beryl containing metasomatic fluorite ores	Fluorite ores with phenakite and xrizoberyl; potentially important deposits	Phenakite xrizoberyl	Cassiterite

of economic value. Table 27.2 summarizes types of beryl deposits of industrial values. Pegmatite ore is most abundant in beryllium deposits. In these deposits beryl is in the form of large crystals. In some of the pegmatitic ore bodies, beryl is found in association with spodumene (spodumene-albite, lepidolite-albite), and has significant economic value for recovery of beryl. From these deposits beryl is recovered using the flotation method.

Hydrothermal-pneumatolytic deposits are relatively complex. With beryl from these deposits, it is possible to recover wolframite, cassiterite, and molybdenite. These deposits have a relatively high concentration of beryl.

27.3 Beneficiation of beryllium containing ores

27.3.1 Beneficiation of beryl

The physiochemical characteristics of beryl as well as other beryllium minerals are similar to that of gangue minerals. Beryl has specific gravity of 2.6 to 3.0 g/cm^3 similar to that of gangue minerals. Therefore, gravity preconcentration and magnetic separation are not applicable to beryllium ore. For beneficiation of beryl three following methods are used in the industrial practice:

1. hand sorting;
2. selective grinding—flotation; and
3. flotation.

The hand sorting is based on color differences between beryl and gangue minerals and is used on the ores that contain large crystals of beryl and also xrizoberyl and izumrud. Sorting is usually done on conveyors or coarse fraction and on rotating tables for finer fraction. Typical flow sheet used for hand sorting is shown in Figure 27.1.

The grade of beryl concentrate obtained by hand sorting is relatively high and ranges from 10% to 12% BeO_2. The recovery of beryl using hand sorting is low (i.e., 25–40% BeO_2) and therefore the tailing from hand sorting is reground and remaining beryl is recovered by flotation.

During hand sorting the important parameter is the proper washing of the crushed ore before sorting.

Selective grinding. This method is based on differences in hardness between beryl and other gangue minerals. Beryl has a hardness of about 8 compared to gangue minerals 3–4 (Mohs scale). The selective grinding is performed in a ball mill with ceramic ball charges. The softer minerals are readily ground using this system while beryl is retained in coarse fractions. A typical selective grinding flow sheet is shown in Figure 27.2.

Sometimes in the ores that contains talc, dolomite, and other soft minerals, by using selective grinding, about 40–50% of the gangue minerals may be removed with beryllium losses of about 10% BeO_2.

27.3.2 Flotation of beryl = general overviews

The primary method for beneficiation of fine beryl is the flotation method. There is an appreciable amount of information in the literature on beryl flotation.

Beryl, however, can be floated using either anionic or cationic collectors in cationic flotation lauryl amine and some primary amines such as hexadecyl amine acetate.

The anionic flotation method involves the use of oleic acid and fatty acid treated with amine. Either of the method is used; hydrofluoric acid, Na_2S, and soda are activators for beryl.

Using oleic acid, beryl is depressed in the presence of sodium silicate and sulfuric acid.

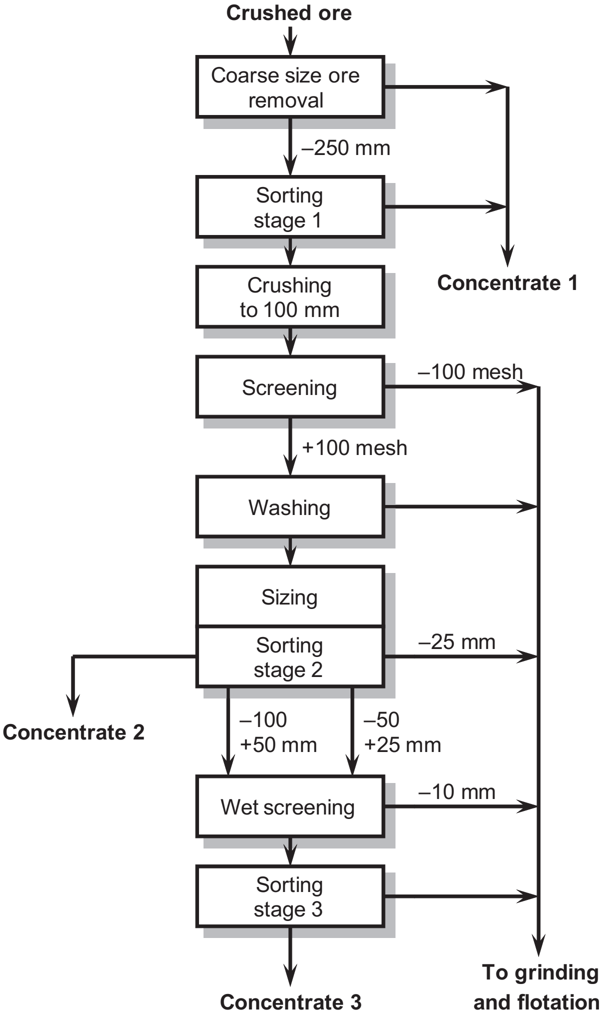

FIGURE 27.1

Typical flow sheet used in hand sorting.

Acid flotation method. In actual fact, this method involves two-stage flotation. In stage 1, mica is floated using amine collectors. The tailing from mica flotation is treated with hydrofluoric acid and deslimed. Beryl is floated from deslimed mica tailings using fatty acid (oleic or a mixture of oleic and linoleic acid). Beryl is usually floated at pH 7.0 to 8.0 in the presence of sodium hydroxide as a pH modifier.

The typical flow sheet used in acid flotation is presented in Figure 27.3.

The bulk flotation method in an acid circuit is also practiced and involves the following steps.

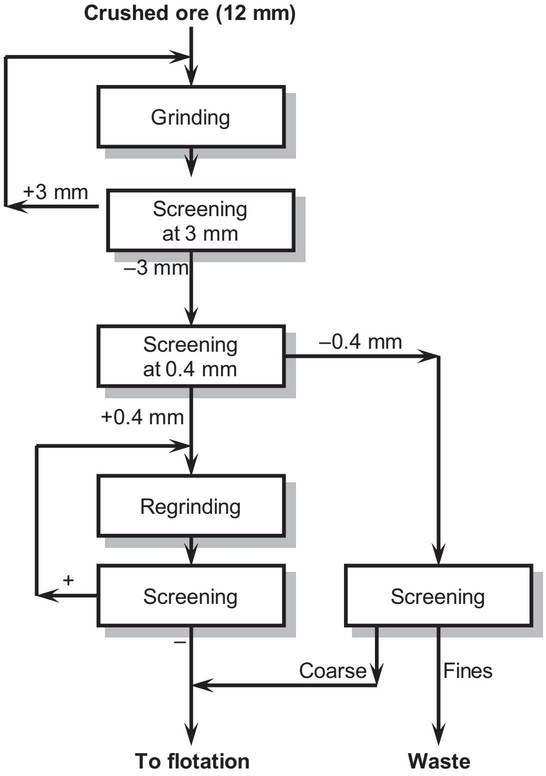

FIGURE 27.2

Flow sheet used in selective grinding.

Initially, mica is floated using amine. The mica tailing is treated with hydrofluoric acid plus sulfuric acid following flotation of beryl and feldspar with lauryl amine collector.

The bulk concentrate is washed in a slightly alkaline pH and beryl is floated with fatty acid. Feldspar, after washing the bulk concentrate does not float with fatty acid. The flow sheet used in the bulk flotation method is presented in Figure 27.4.

With this method, besides beryllium concentrate, silica and feldspar concentrates are produced. In the ore containing amfibol (aktinolit, termolit) calcium, magnesium, and ambligonite (LiO_2) are all floated with beryl in a bulk concentrate. In such cases the bulk concentrate is treated with sodium hydroxide and sodium silicate at elevated temperature (85 °C), following BeO flotation with anionic collector. Amphibole is well depressed using the above method.

Alkaline flotation of beryl. The flotation method of beryllium ores with alkaline pretreatment in a number of cases is similar to that used in flotation of spodumene. Alkaline pretreatment promotes activation of beryl; peptization of slimes acid depression of gangue minerals.

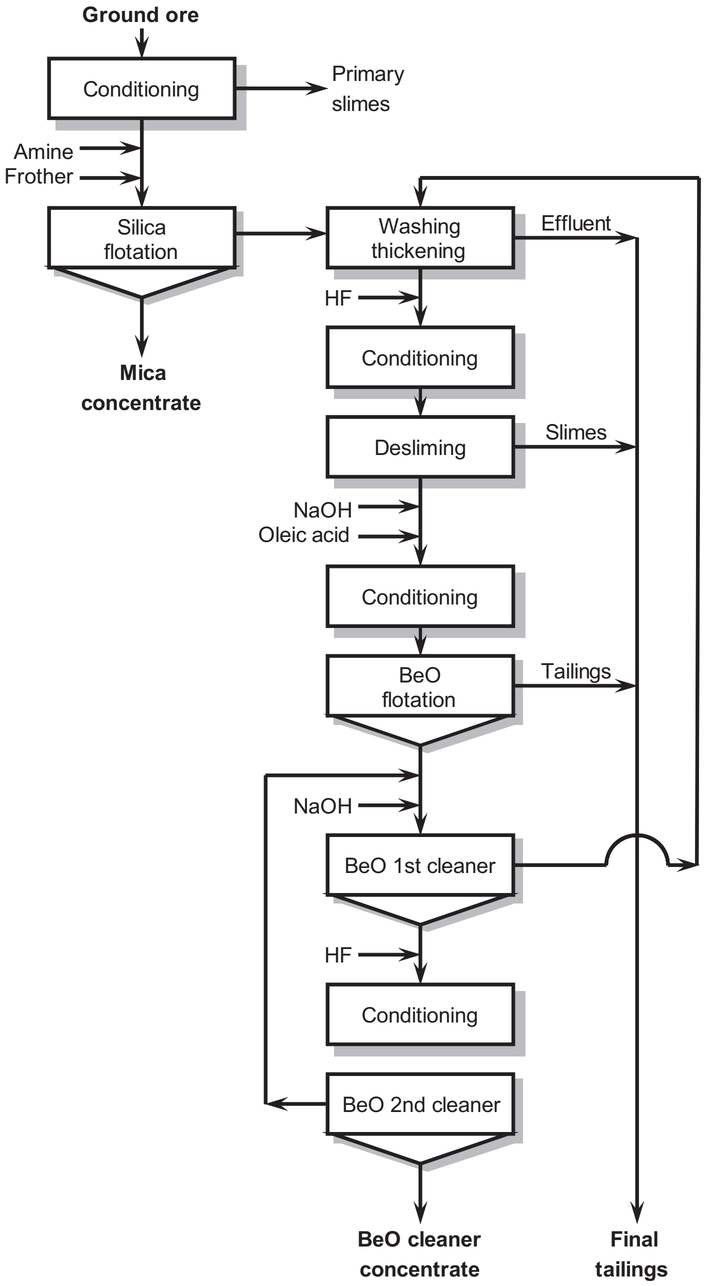

FIGURE 27.3

Typical flow sheet used in acid flotation.

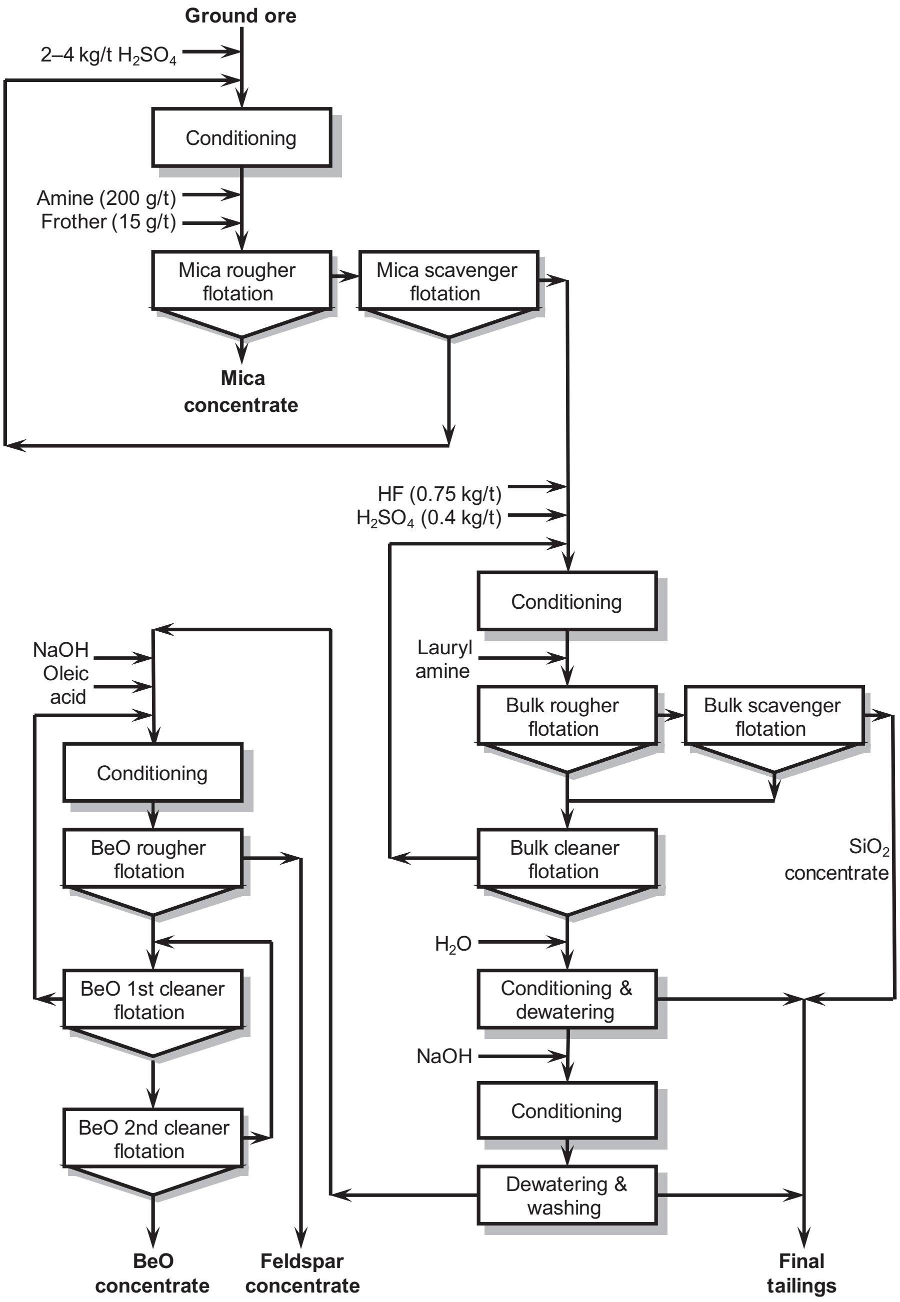

FIGURE 27.4

Typical flow sheet using the bulk flotation method.

Alkaline is added during grinding for high pulp density conditioning.

The ore treated at Bik-Auori (US) containing beryl, feldspar, quartz, orthoclas with a little garnet and iron oxide is treated using an alkaline pretreatment method. The ground deslimed ore is treated with 2.5 kg/t NaOH after which the pulp is washed by dilution and thickening. Beryl is floated using fatty acid made of koko oil. The rougher concentrate is cleaned three times without reagents. From the ore containing 1.3% BeO, a concentrate assaying 12.2% BeO at 75% BeO recovery was produced. Flotation tailings assayed 0.01% BeO but most of beryl losses occurred in a slime fraction (i.e., 21% BeO).

When ores contain tourmaline and garnet with flotation properties better than beryl, it is possible to prefloat tourmaline and garnet before beryl flotation using small quantities of fatty acid. The tailings from tourmaline and garnet prefloat are treated with either NaOH or Na_2S and washed before beryl flotation. Beryl flotation is performed using oleic acid at pH 9.5. The generalized flow sheet using the above method is shown in Figure 27.5.

For depression of gangue minerals in some cases, Na_2S is used, which has a depressing effect on quartz, feldspar, and mica. In most cases using the alkaline method, the pulp is deslimed before beryl flotation.

In some cases the pulp is heated to 85 °C before beryl flotation, usually during beryl flotation from bulk concentrate.

The alkaline flotation method has an advantage over the acid flotation method due to the fact that the use of HF and H_2SO_4 is not required. In addition it is more cost-effective.

The alkaline beneficiation method is most effective for ores that contain not only quartz and feldspar but also talc chlorites and carbonaceous gangue. Talc, chlorite, and carbonaceous gangue are first prefloated, followed by pulp pretreatment with NaOH; desliming and beryl is floated using a fatty acid collector at pH 8.5–9.

27.3.3 Flotation of beryl from pegmatite ores

Development testwork on beryllium flotation from pegmatite ores has been carried out over a considerable period of time [3–5]. A large portion of the world beryl production comes from pegmatite ores. The pegmatite ore containing beryl also contains feldspar, mica, spodumene, and ambligonite, some of which have similar flotation properties as beryl.

In the research studies on the ore containing quartz, feldspar, mica, and beryl, the two following flotation methods were investigated.

Method 1. This method consists of conditioning ground deslimed ore at 50% with 3000 g/t Na_2S followed by heating pulp to 85 °C with 300 g/t oleic acid. The pulp is then diluted and beryl is floated.

Method 2. This method employs petroleum sulfonate as beryl collectors. Initially mica was recovered using tallow amine acetate at pH 3.5 followed by beryl flotation at pH 2.2 using a petroleum sulfonate collector. The results obtained using two flotation methods are presented in Table 27.3.

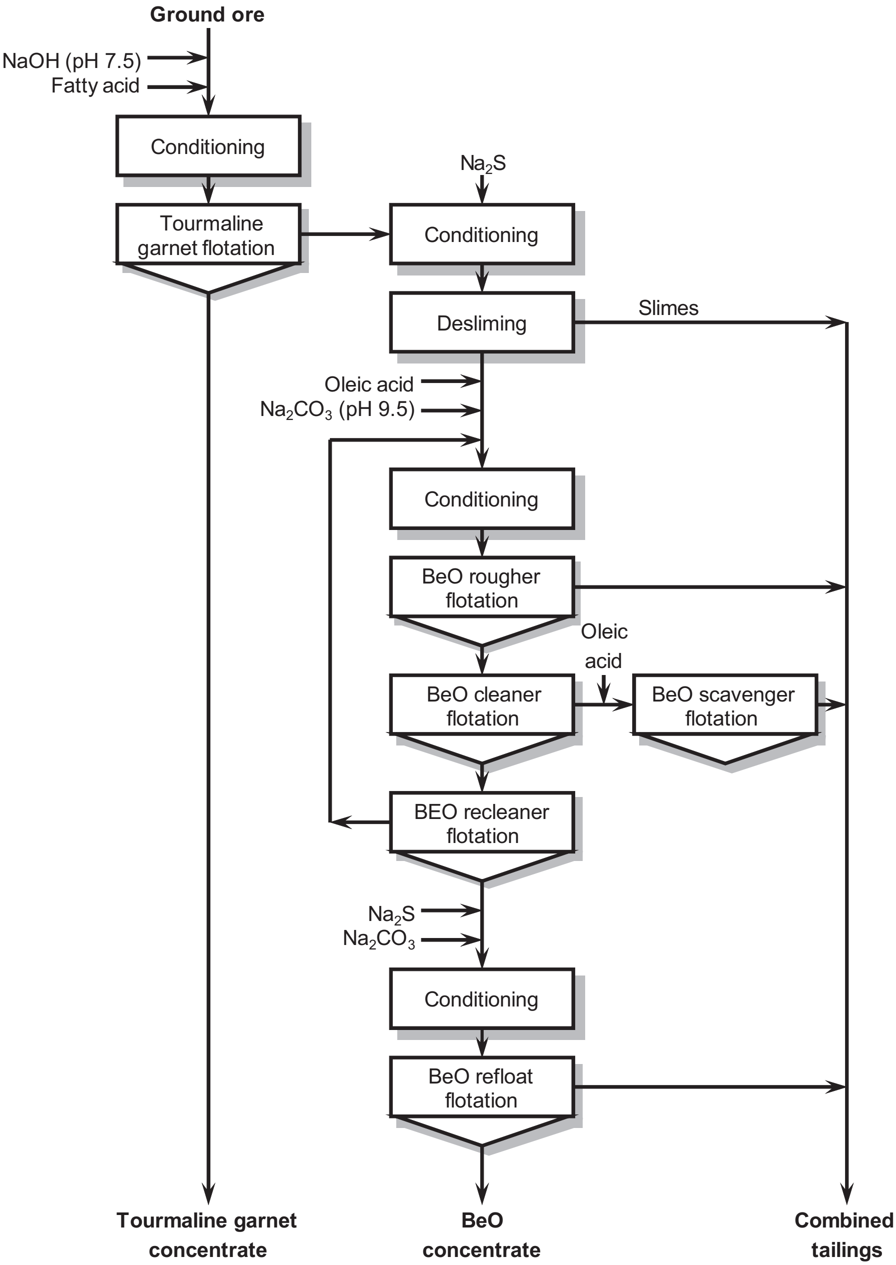

FIGURE 27.5

Flow sheet used in beneficiation of beryl from the ores that contain tourmaline, garnet, mica, quartz, and feldspar.

Table 27.3 Beryl Metallurgical Results Using Two Different Methods

Flotation Method	Product	Wt %	Assay % BeO	Recovery % BeO
Method 1 Na_2S, heat (80 °C) Oleic acid	1 Beryl Cl. concentrate	2.8	8.45	85.2
	Beryl Cl. tail	1.8	0.34	1.1
	Beryl rough tail	84.6	0.02	6.0
	Slimes	10.8	0.20	7.7
	Head (calc.)	100.0	0.28	100.0
Method 2 Mica prefloat H_2SO_4 = pH 2.2 Petroleum sulfonate	Beryl clean concentrate	5.79	4.44	76.7
	Beryl rough tail	41.31	0.04	5.0
	Mica concentrate	42.18	0.09	11.3
	Slimes	10.12	0.23	7.0
	Head (calc.)	100.0	0.374	100.0

The major problem with the use of sulfonate collectors is that in the presence of Ca and Fe ions random activation and depression occurs. The use of hexametaphosphate has a positive effect on beryllium flotation.

Another method examined on Rapid City (US) ore involves two-stage flotation.

In the first stage mica was floated using amine at pH 3.5, followed by reconditioning mica tailings with HF or NaF + H_2SO_4 and bulk beryl/feldspar flotation with extra amine additions.

From the bulk concentrate, amine was removed using hypochlorite, and after subsequent washing beryl was floated using petroleum sulfonate collectors at pH 2.5. Studies carried out on the ore that contains heavy minerals have shown that the mixture of NaF:dextrin (1:1) would selectively float heavy minerals while beryl was depressed. Figure 27.6 shows the effect of pH on the flotation of different minerals using a mixture of NaF dextrin and oleic acid as a collector.

The tailing from heavy minerals was conditioned with HF (700 g/t) at pH of 2.5–3.5 and then washed. The washed pulp was conditioned with 150 g/t NaF and 200 g/t oleic acid followed by beryl flotation. The results obtained using this method ore are shown in Table 27.4.

Another method suitable for beryl recovery from the ore that contains spodumene is the alkaline bulk spodumene beryl flotation method followed by spodumene beryl separation. This treatment method is illustrated in Figure 27.7.

The metallurgical results obtained in a continuous pilot plant operation are shown in Table 27.5.

27.3.4 Flotation of bertrandite and phenacite

There are several deposits of the ore deposits in United States, Canada, and Norway that contain phenacite as a main beryllium mineral and bertrandite to a lesser amount. These deposits have different mineral composition, and can be divided into three major groups.

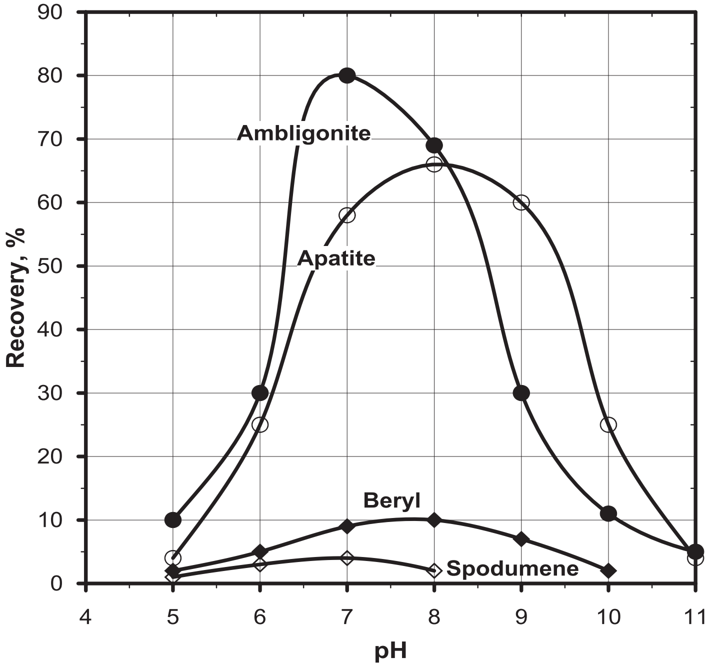

FIGURE 27.6

Effect of pH on different mineral flotation and beryl using NaF/dextrin mixture (10 mg/l) and 150 g/t oleic acid.

Table 27.4 Metallurgical Results Obtained Using Two-Stage Flotation Method

Product	Wt %	Assays % BeO	Recovery % BeO
Beryl concentrate	1.6	10.87	82.2
Beryl clean tail	0.8	0.40	1.5
Beryl rougher tail	85.9	0.01	4.1
Heavy minerals	1.7	0.52	4.2
Primary slimes	9.5	0.17	7.6
Washing slimes	0.5	0.18	0.4
Head (calc.)	100.0	0.21	100.0

These are:

1. Ore that contains phenacite and bertrandite with the gangue is composed chiefly of calcite, fluorite, and mica. Typical examples of these deposits are Mount Wheeler, Nevada, U.S. and Mount Antero Co. U.S.
2. Ore that contains phenacite, Rare Earth Oxides (REO), and yttrium with the gangue is composed of feldspar, iron oxides, mica, and silica. An example of this ore type is Thor Lake, Northwest Territories, Canada.
3. Ore that contains phenacite with gangue is composed of feldspar on quartz.

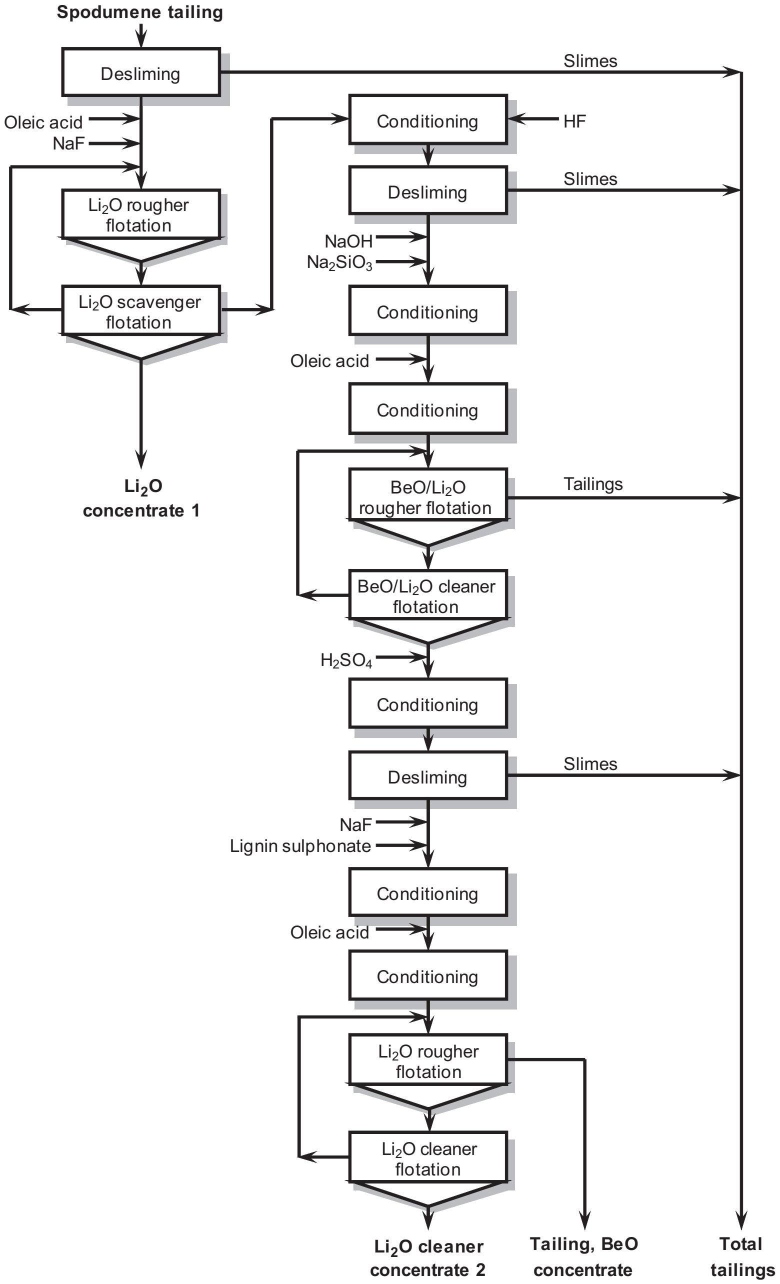

FIGURE 27.7

Flow sheet used for recovery of spodumene and beryl from Foot Mineral Company Spodumene Flotation Tailing.

Table 27.5 Metallurgical Results Obtained Using Bulk Spodumene/Beryl Alkaline Flotation Method

Product	Wt %	Assays %		% Distribution	
		BeO	Li_2O	BeO	Li_2O
Beryl concentrate	1.2	4.12	2.60	71.1	6.9
Spodumene concentrate	1.7	0.42	6.22	10.3	23.4
Hydro separation O/flow.	0.1	0.29	0.51	0.4	0.1
Thickener O/flow.	0.1	0.15	0.40	0.2	0.1
Beryl/Spodumene bulk concentrate	3.1	1.84	4.44	82.0	30.5
Beryl/Spodumene tailing	85.0	0.011	0.10	13.5	18.8
Spiral class O/flow.	4.4	0.01	0.14	0.6	1.4
Spodumene scavenger concentrate	3.6	0.061	5.85	3.1	46.7
Second hydrosep. O/flow.	3.9	0.014	0.30	0.8	2.6
Feed	100.0	0.069	0.45	100.0	100.0

27.3.4.1 Flotation of bertrandite and phenacite from Mount Wheeler ore U.S.

Detailed research work on this ore was conducted by the U.S. Bureau of Mines [6]. The studies were conducted on different ore grades assaying 0.47, 0.78, and 4.17 BeO.

The procedure for selective flotation of the beryllium minerals from the gangue minerals involves closely controlled preconditioning with sodium fluoride and sodium hexametaphosphate. Collector used was a mixture of oleic acid with kerosene fuel oil or turpentine.

The grade and recovery of beryllium from this ore was affected by (1) quantities of HMP, (2) the HMP conditioning time, (3) collector conditioning time, and (4) quantities of NaF. The effect of HMP conditioning time on beryllium flotation is illustrated in Table 27.6.

Table 27.6 Effect of HMP Conditioning Time on Beryllium Grade and Recovery

HMP Conditioning Minutes	Concentrate Assays % BeO	Recovery % BeO
10	7.6	47
20	14.5	77
30	16.5	75
40	9.3	89
50	8.0	90
60	7.0	91

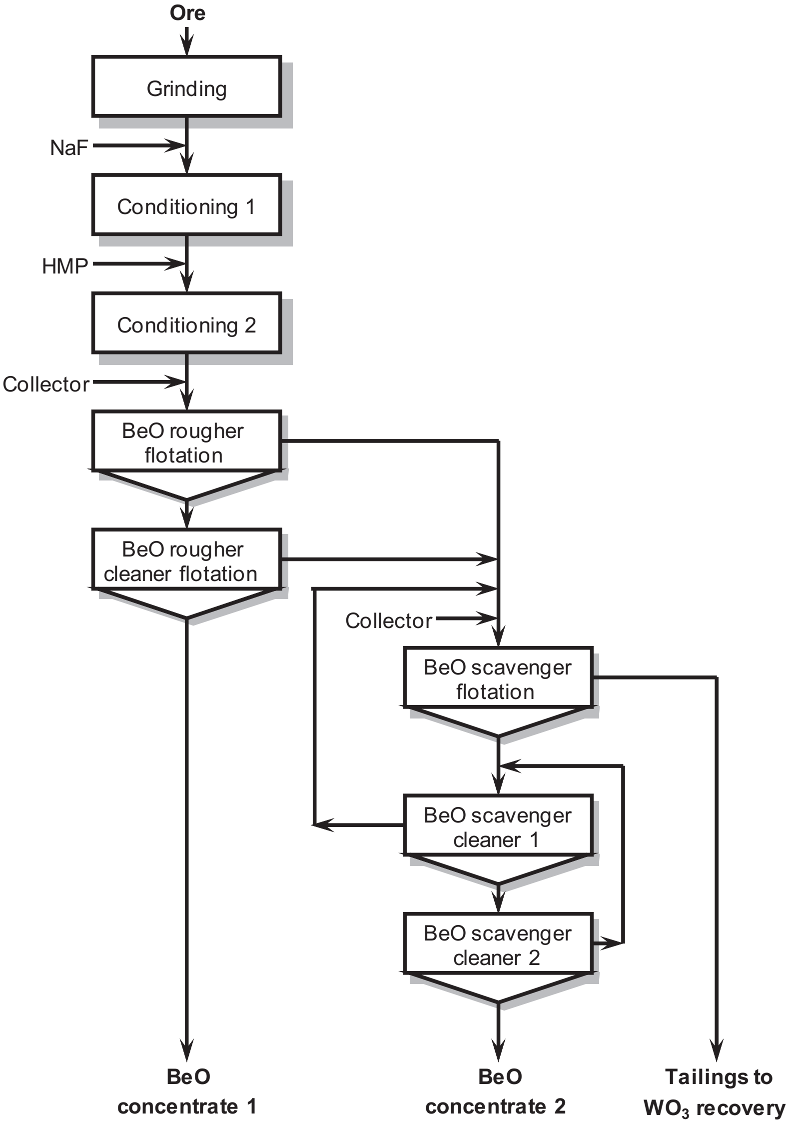

FIGURE 27.8

Flow sheet developed for beneficiation of Mount Wheeler ore.

These data have indicated that optimum conditioning time is about 30 min. Typical flow sheet for beneficiation of bertrandite phenacite from Mount Wheeler is shown in Figure 27.8. The reagent scheme and metallurgical results are presented in Table 27.7(a and b).

Table 27.7 Reagent Scheme and Metallurgical Results Obtained on Mount Wheeler Ore

(a) Reagent Scheme

Reagent	Additions, g/t
Sodium fluoride (NaF)	2100
Hexametaphosphate (HMP)	550
Collector 1	500

(b) Results

		Assays %		Distribution
	Wt %	BeO	$CaCO_3$	% BeO
Concentrate 1	1.66	24.8	9.1	54.1
Concentrate 2	1.18	15.6	12.3	24.2
Combine concentrates	2.84	21.0	10.4	78.3
Final tail	97.16	0.17	–	21.7
Head (calc.)	100.0	0.76	–	100.0

Collector 1 is composed of four parts of oleic acid and four parts of terpene dissolved in 92% ethyl alcohol.

The results obtained in a continuous pilot plant operation are considered satisfactory.

27.3.4.2 Flotation of phenacite from complex beryllium, yttrium and REO ore

During 1980 an extensive research work was performed [7,8] on a complex beryllium, yttrium, and REO ore with the objective of recovering high-grade phenacite concentrate. The Thor Lake (Canada) phenacite ore also contains appreciable amounts of yttrium and rare earth elements. The main gangue minerals present in the ore were feldspar, mica, various alumosilicates, quartz, and minor amounts of calcite, dolomite, and magnetite.

Extensive laboratory development testwork was performed in which a number of optional reagent schemes were examined including bulk phenacite feldspar flotation followed by separation using sulfonate collectors for phenacite flotation. From the reagent schemes examined, acid pretreatment followed by phenacite flotation using fatty acid gave the best metallurgical results.

The treatment flow sheet developed for beneficiation of phenacite is shown in Figure 27.9.

This flow sheet was used in the continuous pilot plant operation.

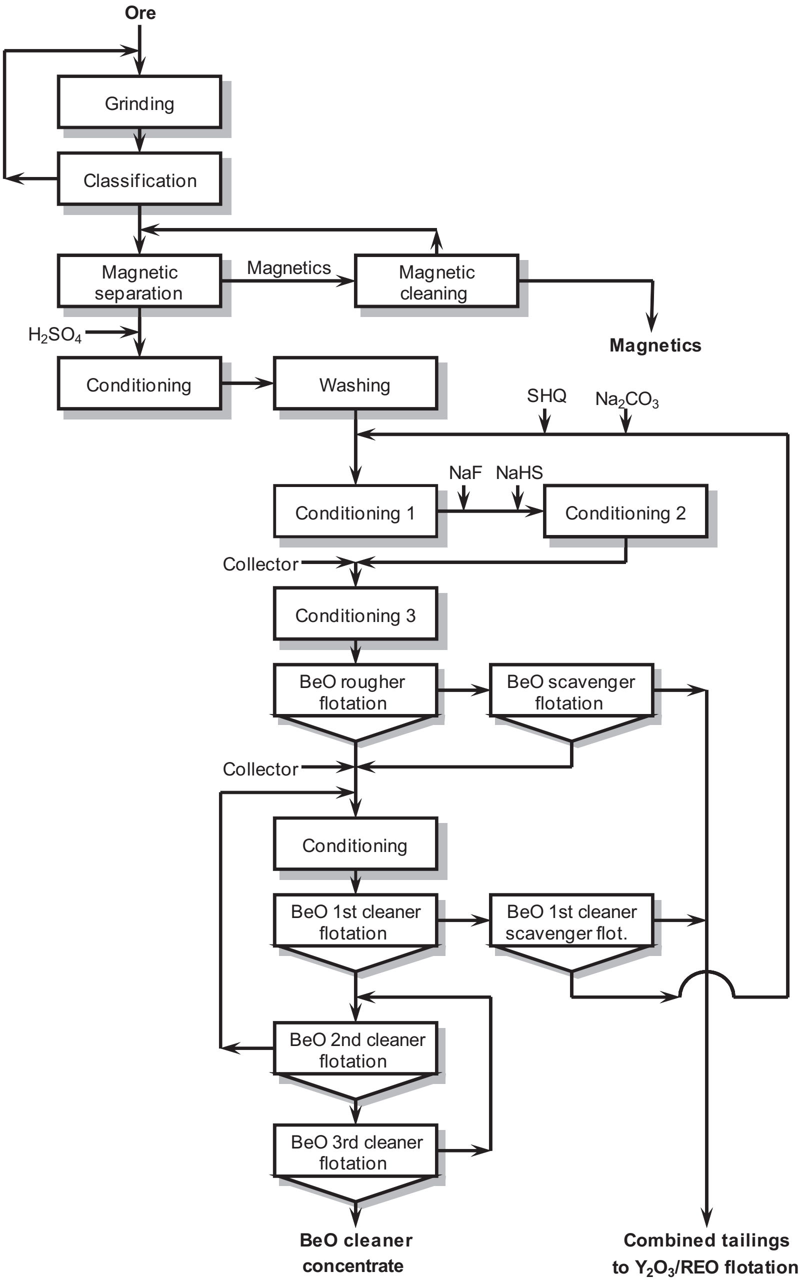

FIGURE 27.9

Flow sheet for beneficiation of phenacite from Thor Lake deposit (Canada).

The final reagent scheme used in the pilot plant is presented in Table 27.8.

The SHQ is a slime dispersant and is composed of a mixture of low molecular weight acrylic acid and sodium silicate.

The metallurgical results obtained in the laboratory and pilot plant are presented in Table 27.9.

The laboratory and pilot plant beryllium metallurgical results were similar.

27.3.5 Operating plants

Most of the operating plants over the years were shut down and only a few plants are now in operation, treating mainly ores that contain beryl using the processes described in this chapter.

Table 27.8 Final Reagent Scheme Developed for Beneficiation of Thor Lake Phenacite Ore

	Additions, g/t		pH	
Reagent	**BeO Concl. + Ro**	**BeO Cleaner**	**Ro**	**Cleaner**
Depressants and Modifiers				
H_2SO_4[a]	1100	–		
Na_2CO_3	1500	60	8.5	5.5
SHQ[b]	170	50		
NaHS	150	80		
NaF	300	200		
MAA (surfactant)				
Collectors				
Fatty acid (emulsified)	500	200		

[a] *Acid pretreatment.*
[b] *Mixture of Lignin sulphonate, starch and silicate.*

Table 27.9 Overall Metallurgical Results Obtained in the Laboratory and the Pilot Plant

			Assays %			% Distribution		
Circuit	**Product**	**Wt**	**BeO**	**Y_2O_3**	**Total REO**	**BeO**	**Y_2O_3**	**Total REO**
Laboratory continuous	BeO Cl. concentrate	2.93	24.9	0.094	0.85	82.5	0.8	0.6
	REO + Y_2O_3 Cl. concentrate	11.13	0.98	2.19	16.35	11.0	74.6	80.2
	Comb. tail	84.93	0.065	0.093	0.085	6.2	24.2	11.8
	Magnetics	1.00	0.26	0.12	–	0.3	0.4	–
	Head (calc.)	100.0	0.90	0.33	–	100.0	100.0	100.0
Pilot plant	BeO Cl. concentrate	4.01	21.1	0.56	0.70	83.3	8.6	5.2
	REO + Y_2O_3 Cl. concentrate	8.65	1.00	1.95	15.30	9.0	61.2	75.3
	Comb. tail	86.12	0.068	0.11	0.22	6.8	29.4	24.4
	Magnetics	1.22	0.68	0.21	–	0.9	0.8	–
	Head (calc.)	100.0	0.91	0.29	–	100.0	100.0	100.0

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CHAPTER

Beneficiation of Lithium Ores

28

CHAPTER OUTLINE

28.1 Introduction

There are several types of lithium minerals of economic values. These include spodumene, lepidolite, amblygonite, zinvaldite, and petalite.

Most of the lithium production comes from spodumene and petalite to a lesser degree, from lepidolite. Lithium in general belongs to a group of light metals with specific gravity of 0.53 g/Cu^3. The chemistry of each of the major lithium minerals is somewhat different. Some of the chemical features of the lithium minerals can be described as follows:

Spodumene: The pure mineral is insoluble in dilute acid and is frequently found in an iron oxide coating; in some cases up to 1% iron is found on mineral surfaces. The removal of surface coating is mandatory for successful spodumene flotation.

Lepidolite: This is also known as lithium mica. Pure mineral is attached but not decomposed by acid. The interlayer potassium is capable of ion exchange which as with other mica frequently occurs with iron salts. This can lead to anionic activation

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00003-8

of the mica and could, under acid flotation conditions lead to activation of other minerals in a flotation pulp.

Petalite: This is insoluble in acid and is a relatively stable mineral. In natural ores it is usually found in a crystalline state. Petalite can be attacked by hydrofluoric acid.

The flotation properties of individual lithium minerals are significantly different and largely dependent on the ore type and mineral composition of the ore.

28.2 Lithium ores and minerals

About 150 different lithium containing minerals are known and only 30 of these contain significant quantities of lithium. They are represented by silicates and phosphates. Also the lithium minerals can exist as carbonates, sulfates, nitrates, wolframites, and others.

Of those, only five lithium minerals listed in Table 28.1 are of economic values.

Spodumene belongs to a silicate group and contains about 8% Li_2O, 64.5% SiO_2, and 27.5% Al_2O_3. Spodumene is usually found in granite-pegmatites in the form of crystals with different sizes and in association with quartz, mica amblygonite, beryllium, and tantalum. Spodumene has a glossy, yellowish, or blue color. During the process of formation of pegmatites, spodumene can be replaced by other minerals like petalite quartz, albite, and muscovite.

Lepidolite and also zinvaldite contain less lithium as compared to spodumene. Lepidolite is usually an unstable mineral, containing Al_2O_3 between 11.3% and 28.8%, SiO_2 from 46.9 to 60.1, Li_2O from 1.5% to 5.5%, and fluorite 9%. Lepidolite contains rubidium up to 3.7% Rb_2O and cesium about 1.5% Cs_2O. The crystal structure is similar to that of muscovite and has a purple color.

Amblygonite is a lithium phosphate that contains up to 10% Li_2O. However, it has a secondary role in the production of lithium due to high phosphorus content. The color of amblyonite is white to greenish. This minerals contains 54% P_2O_5, 34% Al_2O_3, and up to 12% F.

Table 28.1 Lithium Minerals of Economic Values

Mineral	Formula	Content % Li_2O		SG, g/Cu^3	Hardness (MoOS)
		Theoretical	Actual		
Spodumene	$LiAl\ [Si_2O_6]$	8.1	4.5–8	3.2	6.5–7
Lepidolite	$KLi1.5Al1.5[Si_3AlO_{10}][F,OH]_2$	5.9	1.2–5.9	2.8–2.9	2–3
Amblygonite	$LiAl(PO_4)(F_1OH)$ or $Li_2O_3.2LiF.P_2O_5.Li_2O$	10.1	8–9.5	3–3.2	6
Zinvaldite	$KLiFeAl[Si_3AlO_{10}][F,OH]_2$	4.13	2–3	2.9–3.2	2–3
Petalite	$(Li,Na)AlSi_4O_{11}$	4.89	2–4	2.39–2.46	6–6.5

Petalite is aluminum silicate and contains up to 4.8% Li_2O, 16.7% Al_2O_3, and 78.4% SiO_2. Petalite is found only in the pegmatite type deposits in the form of aggregates and seldom has crystalline structure. Typically, those ores contain lepidolite, amblygonite, and pollucite.

Zinvaldite as lepidolite belongs to an isomorph group of luotite–lepidolite complexes. Zinvaldite usually contains wolframite, cassiterite, fluorite, and topaz. Zinvaldite contains up to 12.5% FeO and it has a low magnetic success ability/success rate.

The industrial types of ores can be divided into three major groups (Table 28.2) including:

- Granito-pegmatite or spodumene pegmatite is a major source of production of spodumene concentrate. Gravito pegmatites can be divided into three subgroups: (1) spodumene pegmatite, (2) spodumene lepidolite pegmatites, and (3) petalite lapidolite pegmatites.
- Pneumatolyte–hydrothermal deposits with amblygonite as the main lithium mineral salt deposit contain lithium salts of chlorite and bromine.

These deposits are found in North America, Europe, South America, and Africa. Africa is a major producer of petalite.

Table 28.2 Industrial Types of Lithium Containing Ores

Ore Types	Lithium Minerals Present	Other Associated Minerals Present	Examples of Ore Bodies
1. Granito pegmatitic: a. Spodumene pegmatites	Spodumene	Trifilite, litiofilite petalite, beryl columbite, tantalite, cassiterite	Kings Mountain (US), Ket Lake, La-Cruz (Canada), Lalin (Spain)
b. Spodumene–lepidolite pegmatites	Spodumene, lepidolite, amblygonite	Pollucite, beryl, tantar, microlite, cassiterite	South Dakota (US), Black Hills (US), Baritec (Sweden)
c. Petalite–l apidolite pegmatites	Petalite, lepidolite, ambligonite	Beryl, tantalite, cassiterite	Karibib (S.W. Africa), Rhodesia, London, Derry (Australia)
d. Lepidolite–pegmatites	Lepidolite	Amblygonite, beryl, tantalite, cassiterite	California (US) separation rapids (Canada)
2. Pneumatolyte–hydrothermal: amblygonite lenses	Amblygonite	Cassiterite	Kocepec (Spain)
3. Salt sediments	Lake sediments	Salts of Na, K, B, Li, etc.	Silverpick Road (US), Neelake Atacama (Chile)

28.3 General overview of beneficiation of lithium ore

The physical–chemical characteristics of lithium minerals are similar to that of gangue minerals (i.e., quartz, feldspar, etc.) and therefore beneficiation of lithium is sometimes a challenging task.

However flotation is a principal method for beneficiation of lithium minerals. In recent years a new technology has been developed for flotation of spodumene, and petalite. Using an innovative technology, a production of high-grade petalite concentrate was achieved (i.e., 4.6% Li_2O) [1].

- *Hand sorting* is another concentration method and is used for the ore where lithium minerals are in the form of large crystals and also utilizes the color difference between lithium and gangue minerals. This process is practical for beneficiation of petalite ores (Zimbabwe, Africa, and China).
- *Heavy liquid separation* is mostly for the beneficiation of spodumene ore. This method is based on specific gravity differences between spodumene (3.2 g/Cu^3) and gangue minerals (2.6–2.7 g/Cu^3). Heavy liquid preconcentration can also be used in combination with flotation.
- *Thermal treatment* (decapitation) is sometimes used for concentration of spodumene ores. The ore is heated to 95–1000 °C, where the spodumene is converted from α to β form in which case spodumene is transferred to powder form and is separated from other minerals either by screening or by air classification.

Magnetic separation is used for recovery of zinvaldite, which contains about 0.5% FeO.

28.4 Flotation properties of different lithium minerals

28.4.1 Flotation properties of spodumene

Flotation properties and selection of flotation methods very much depends on the type of gangue minerals present in the ore. Flotation properties of spodumene was also affected by the presence of heavy metals cations (i.e., iron). Over the years extensive research work has been conducted on various ore types. Studies were conducted on beryllium-spodumene ore [2]. In these studies oleic acid was used to float spodumene from beryl. The method comprised of pulp pretreatment with sodium hydroxide followed by desliming before collector conditioning at elevated temperature (80–85 °C). Using this method it was possible to selectively float spodumene from beryl and other gangue minerals.

During beneficiation of various spodumene containing ores, pulp pretreatment before spodumene flotation is very important. This has been confirmed by a number of researchers [3]. Pretreatment of pulp is performed by two methods, these are: (1) conditioning pulp at 50–60% solids in the presence of 0.5 to 1 kg/t NaOH for 20–30 min. The NaOH was added in stages at 10 min intervals. After surface treatment the pulp was deslimed following spodumene flotation using oleic acid (400–600 g/t). (2) The use of Na_2S in the pretreatment stage also gave good metallurgical results in the subsequent flotation stage. Oleic acid was found to be the best collector for spodumene flotation.

With South Dakota ore (US) using NaOH pretreatment followed by desliming and spodumene flotation using oleic acid concentrate grade assaying 7.2% Li_2O at 75% recovery was achieved in a pilot plant test.

During the treatment of pegmatite ore that contained spodumene, mica, feldspar, and quartz, two methods have been developed by Cytec.

Cytec research laboratories. In both methods the ground ore was scrubbed at 20% solids in the presence of 2 kg/t NaOH for 20 min. The scrubbed pulp was deslimed.

In one method an initial removal of mica was carried out using amine collector at pH 2.5 to 3.0. The mica tailing is dewatered followed by conditioning with oleic acid at 50% solids. After collector conditioning, the pulp was diluted to 20% solids and spodumene rougher flotation was performed followed by two cleaning stages. Using this method a concentrate grade assaying 5.0% Li_2O at only 45% recovery was achieved.

The second method examined was more successful, involving first spodumene flotation following acid conditioning of the deslimed pulp at 64% solids with 500 g/t oleic acid. The rougher float was performed at about 28% solids. Rougher concentrate was cleaned twice also in the acid circuit. Using this method, a concentrate grade assaying 7.2% Li_2O at 90% Li_2O recovery was achieved.

Another pretreatment method used for recovery of spodumene from weathered pegmatite involves grinding the ore in the presence of NaF soda ash and Cytec depressant 610 (modified sulfonate) followed by scrubbing with extra additions of NaF and depressant 610 and desliming. The deslimed pulp was conditioned with Aero 765 (mixture of oleic and linoleic acid) and spodumene rougher and two cleaning stage was performed. Using this method about 80% Li_2O was recovered in a concentrate assaying 5% Li_2O.

In treatment of North Carolina beryl-containing pegmatite, a method involving conditioning ground ore with NaF and liquid sulfonate followed by washing and desliming was performed. The deslimed pulp was conditioned with oleic acid and spodumene was floated at pH between 6.5 and 8.0. Using this method about 80% Li_2O was recovered at a concentrate grade assaying 6.5% Li_2O. The method involving reverse gangue flotation was examined on the ore containing quartz, feldspar, and mica using cationic collector (Armac T-lauryl amine acetate) in conjunction with sodium hydroxide dextrin and pine oil. Using this method most of the mica and quartz together with a portion of feldspar was recovered and cell product containing about 6% Li_2O at 78% Li_2O recovery was obtained.

28.4.2 Research and development of the new spodumene flotation system

During the 1980s and early 1990s extensive research work was carried out on various spodumene containing ores from Canada [4,5]. As a result, a highly effective collector system has been developed, which is capable of producing a high concentrate grade and high recovery. These collectors are mixtures of petroleum sulfonate (R800 series from Cytec) and fatty acid (mixture of oleic and linoleic acid, pine oil, and MIBC (frother)). Each of these collectors is known as a collector from the LR series.

Table 28.3 shows the composition of several of the collectors from the LR series.

Collector LR19 was developed and introduced in the Tanco Plant (Manitoba, Canada) for production of high-grade spodumene ore from pegmatite containing quartz, microcline, and albite. The effect of collector LR19 on spodumene flotation is illustrated in Figure 28.1.

Table 28.3 Composition of Collectors from LR Series

	% Present in the Mixture		
Reagent	**Collector LR 15**	**Collector LR 17**	**Collector LR 19**
Tall oil Arizona D30LR	–	61.6	62
Oleic acid	62	–	–
Petroleum sulfonate R801	–	–	27
Petroleum sulfonate R827	27	27.7	–
Kerosene	8	8.2	9
Pine oil	5	2.5	2

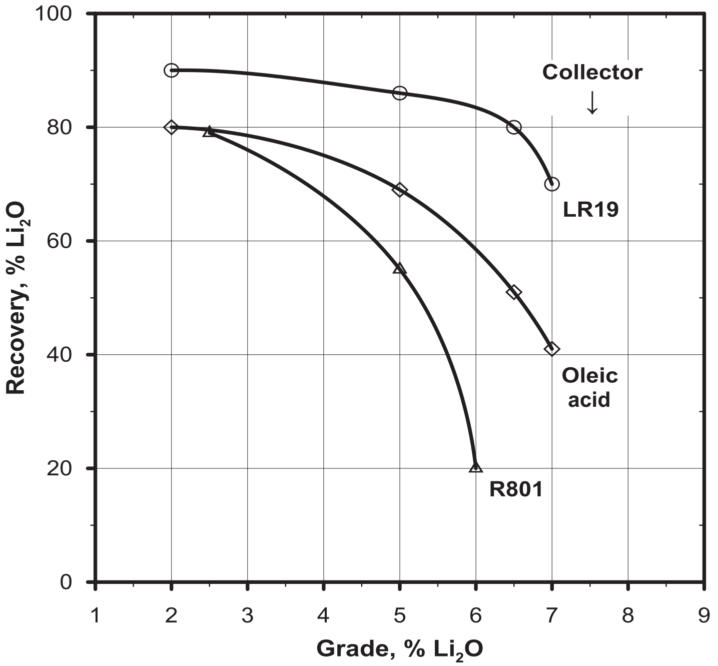

FIGURE 28.1

Effect of different collectors on spodumene flotation from Tanco pegmatite.

28.4.3 Flotation properties of lepidolite

Lepidolite or lithium mica has quite a large flotation area normally with cationic collector (dodecylamines), which ranges from pH 2.5 up to pH 11.0.

Pretreatment of lapidolite with NaOH has no beneficial effect as that observed with spodumene. Starches and Na_2S are depressants for lepidolite. Pretreatment of the ore with oleic acid improves flotation of lepidolite when using sodium oleate as a collector. When using octadecylamine page 17 as a collector, sodium silicate and Li_2SO_4 acts as a lepidolite activator.

From the amines examined from various studies, it was found that hexadecyl amine acetate (Armac 16D–Akzo Nobel) proved to be the most effective collector when floating lepidolite at pH 3.5.

Pulp density was found to be important. Flotation at pulp density below 20% solids had a negative effect of lepidolite flotation. The optimum pulp density is about 25% solids. Another collector developed by South African National Institute of Metals involves a mixture of amine and petroleum sulfonate collector (1:1 ratio). Using this collector and floating lepidolite at pH 9.0, a concentrate grade of 3.8% Li_2O at 80% recovery was achieved.

Flotation properties of lepidolite that contains rubidium is somewhat different from that of pure lepidolite. The maximum recovery of rubidium lepidolite is achieved at pH 2.5 using amine acetate (Armac T). Figure 28.2 shows the effect of pH on lepidolite recovery.

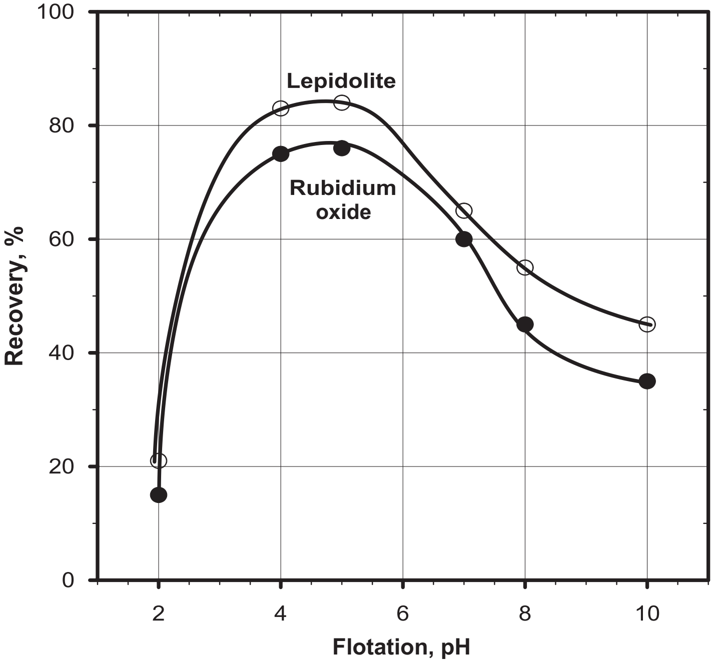

FIGURE 28.2

Effect of pH on rubidium lepidolite recovery using Armac T collector.

Table 28.4 Effect of pH on Petalite Flotation from Separation Rapids (Canada) Pegmatite Ore Using Dodecylamine Collector

Collector Additions, g/t	Flotation pH	Cleaner Concentrate		Rougher Concentrate	
		Assays % Li_2O	Distribution % Li_2O	Assays % Li_2O	Distribution % Li_2O
450	2.0	2.20	45	1.5	56
450	4.0	2.33	42	1.4	55
450	8.0	2.18	35	1.2	50
700	2.0	2.40	50	1.7	66
700	4.0	2.35	52.0	14.6	64

In these experiments a concentrate grade of 3.6% Li_2O at 85% Li_2O recovery was achieved. Concentrate assayed 3.2% Rb_2O_3.

28.4.4 Flotation properties of petalite

Very little data exist in literature on flotation of petalite. It has been claimed that good flotation of petalite was obtained with the dodecylamine collector, with very little sensitivity to change in pH between 2.0 and 11.0. This is not the case in treating complex pegmatite ores that contain feldspar, lepidolite, mica, and albite. With this ore using dodecylamine as the collector and with pH varying between 2.0 and 8.0 no selective flotation of petalite was achieved [6]. Table 28.4 shows metallurgical results obtained in the laboratory using dodecylamine and various pH.

Extensive research conducted on the same ore resulted in the development of a new treatment process that produces a concentrate grade of 4.7% Li_2O at 85% petalite recovery [7]. The reagent scheme and the metallurgical results obtained on complex petalite ore are shown in Table 28.5(a and b).

In these experiments first mica is recovered followed by spodumene flotation. This was lithium mica and also contains significant quantities of rubidium. The flow sheet used in these experiments is shown in Figure 28.3 below.

28.5 Plant practices in beneficiation of lithium bearing ores

The lithium ores and operating plants are found in Australia, Canada, and United States. In the other parts of the world lithium is found in China, Africa (petalite ore), and Brazil. Treatment options of spodumene and petalite largely depends on the gangue composition present in the ore. If the ore contains mica and talc, then these are floated ahead of spodumene. Several processing plants of importance are deslimed in this section.

Table 28.5 Reagent Scheme and Metallurgical Results Obtained on Petalite Ore Using New Process

(a) Reagent Scheme

Reagent	Mica Flotation	Spodumene Flotation	Petalite Flotation
HCl	450	–	–
ARMACT (Akzo Nobel)	150	–	–
NaOH	–	500	–
Tall oil D40 LR (emulsified)	–	800	–
HF	–	–	500
H_2SO_4	–	–	–
NaCl/KCl brine (1:1)	–	–	10%
AMG93 (Akzo Nobel)	–	–	380

(b) Metallurgical Results

		Assays %				% Distribution			
Product	**Wt %**	**Li_2O**	**Al_2O_3**	**K_2O**	**Na_2O**	**Li_2O**	**Al_2O_3**	**K_2O**	**Na_2O**
Mica concentrate	15.91	2.04	24.4	6.17	2.23	21.8	24.4	39.1	9.0
Spodumene concentrate	3.01	4.02	21.3	0.40	0.48	8.1	4.0	0.5	0.4
High-grade petal. concentrate	10.57	4.61	16.4	0.28	0.37	36.2	11.0	1.2	1.0
Low-grade petal. concentrate	9.27	4.01	16.8	0.36	0.57	24.9	13.6	5.5	10.1
Low-grade petal. Ro. concentrate	20.39	1.99	15.2	1.45	2.29	27.2	22.9	15.7	26.2
Petalite Ro. tail	47.42	0.17	12.7	2.46	5.55	5.5	34.0	40.2	60.6
Slimes	2.70	1.74	16.3	2.54	3.04	2.9	26	2.5	2.0
Head	100.00	1.53	15.8	2.57	3.78	100.0	100.0	100.0	100.0

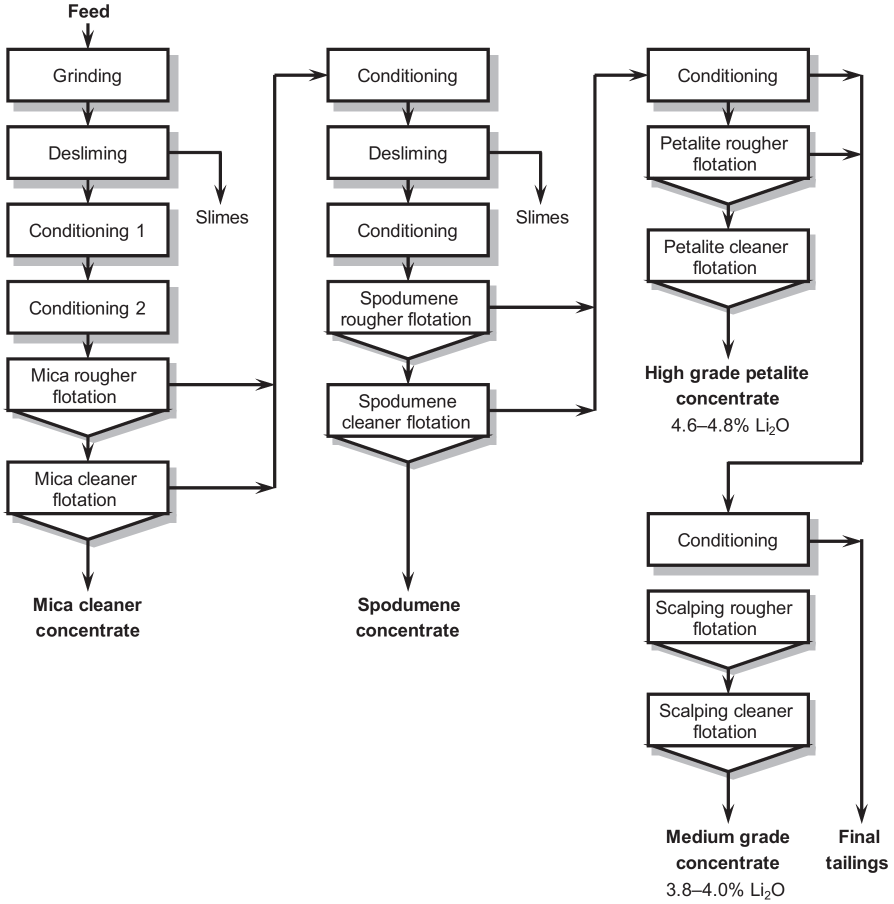

FIGURE 28.3

Flow sheet for beneficiation of petalite from complex ores using flotation.

28.5.1 Bernic Lake—Manitoba, Canada

The Bernic Lake ore is relatively complex and variable within the ore body. The main minerals include quartz, feldspars, microcline, albite, and lepidolite. Major lithium minerals are spodumene with some amblygonite. The amblygonite represents a problem in recovery of spodumene as this mineral contains phosphorus, which is an impurity in production of high-grade spodumene. Initial development work started in 1978, which included pilot plant testing. Plant production was started in 1984. In the treatment flow sheet, heavy media separation was included [8]; also preflotation of amblygonite before lithium flotation. The plant flow sheet is illustrated in Figure 28.4.

The metallurgical results obtained with heavy media separation are shown in Table 28.6. Approximately about 35.9% weight was rejected in the float product which contained only 3.1% Li_2O of the feed. The triflow was used for heavy media separation.

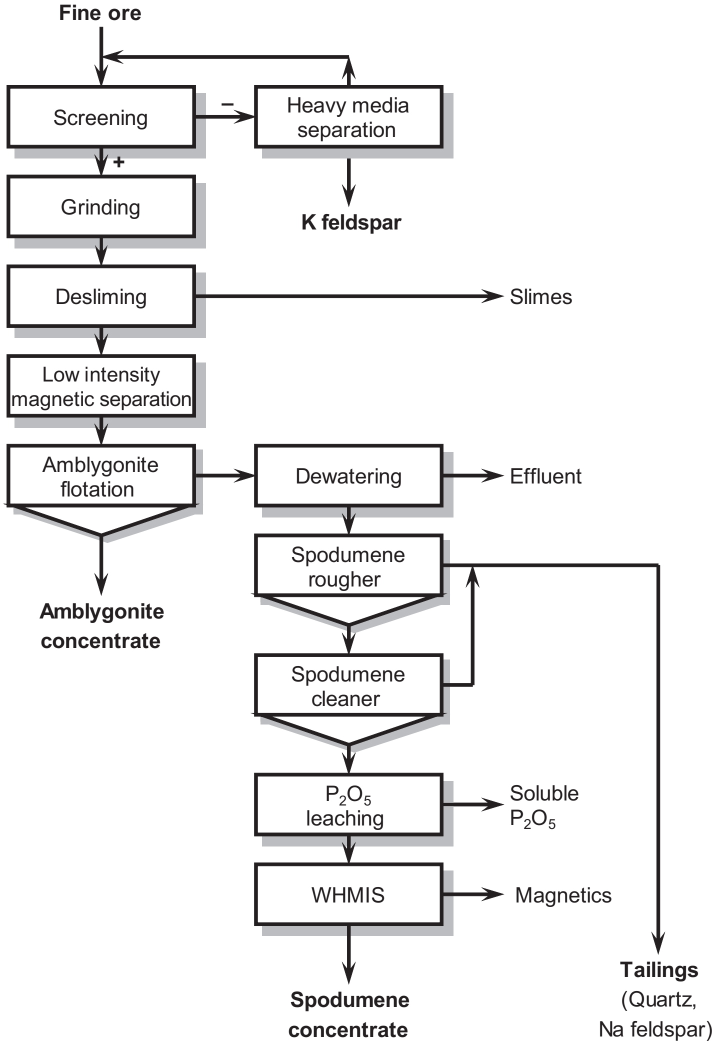

FIGURE 28.4

Bernic Lake lithium flow sheet. WHMIS = High gradient Magnetic Separation

The heavy media feed size was minus 12 mm plus 0.5 mm and the heavy media density was 2.7.

The amblygonite flotation involves conditioning with starch to depress spodumene and starvation addition of emulsified tall oil. In the spodumene flotation, the Na_2CO_3 was used as a pH modifier and collector LR19 (described in Table 28.3). The spodumene rougher and cleaning was performed at pH 9.5. The flotation metallurgical results from the heavy media product are summarized in Table 28.7.

Table 28.6 Plant Heavy Media Separation Test Results

Product	Wt %	Assays %			% Distribution		
		Li_2O	Na_2O	K_2O	Li_2O	Na_2O	K_2O
Sink 1	53.4	5.41	0.38	0.14	83.0	23.2	2.2
Sink 2	10.7	4.50	0.53	0.31	13.9	6.5	10
Combined sinks	64.1	5.26	0.41	0.17	96.9	29.7	3.2
Float	35.9	0.30	1.71	9.15	3.1	70.3	96.8
Feed	100.0	3.48	0.87	3.39	100.0	100.0	100.0

Table 28.7 Projected Plant Metallurgical Results

Product	Wt %	Assays %		% Distribution	
		Li_2O	P_2O_5	Li_2O	P_2O_5
Li_2O Cl. concentrate	37.46	7.10	0.05	82.4	10.05
P_2O_5 comb. concentrate	2.74	5.28	4.47	4.49	65.88
Li_2O Cl. tails	11.70	2.64	0.05	10.02	3.28
Scavenger tail	47.39	0.18	0.08	2.65	20.36
Slimes	0.77	2.03	0.11	0.48	0.43
Feed	100.00	3.22	0.20	100.00	100.00

The concentrate grade on average was about 7.2 Li_2O and sometimes reached about 7.7% Li_2O.

28.5.2 Lithium, Australia—Greenbushes operation

The Greenbushes is a major producer of lithium in the world. There are two ore bodies including tantalum/niobium and tin and the lithium ore body. The ore reserves are about 30 million tonnes, containing at least 7 million tonnes at 4.0% Li_2O [9].

The processing plant produces glass-grade concentrate and high-grade concentrate. The processing flow sheet is shown in Figure 28.5.

The ore is crushed to 16 mm nominal size. The ore is fed to a ball mill. The ball mill discharge is classified into 15 columns, where 250 μm fraction is removed to provide feed for desliming and flotation.

The plus 250 μm fraction is screened on 800 μm screen. The plus 800 μm material is recycled to a ball mill and plus 800 μm fraction is subjected to a magnetic separation. The nonmagnetic fraction is glass grade spodumene assaying about 6.5% Li_2O. The minus 250 μm fraction is deslimed to remove minus 20 μm slime followed by bulk spodumene tourmaline flotation using fatty acid collectors and soda ash for pH control (pH of 7.0–7.5). The bulk concentrate is treated by gravity followed by magnetic separation to remove tourmaline. Magnetic separation is done at 0.9 T magnetic field strength.

The concentrate grade after magnetic separation assayed 7.5–7.7% Li_2O and less than 0.1% Fe_2O_3.

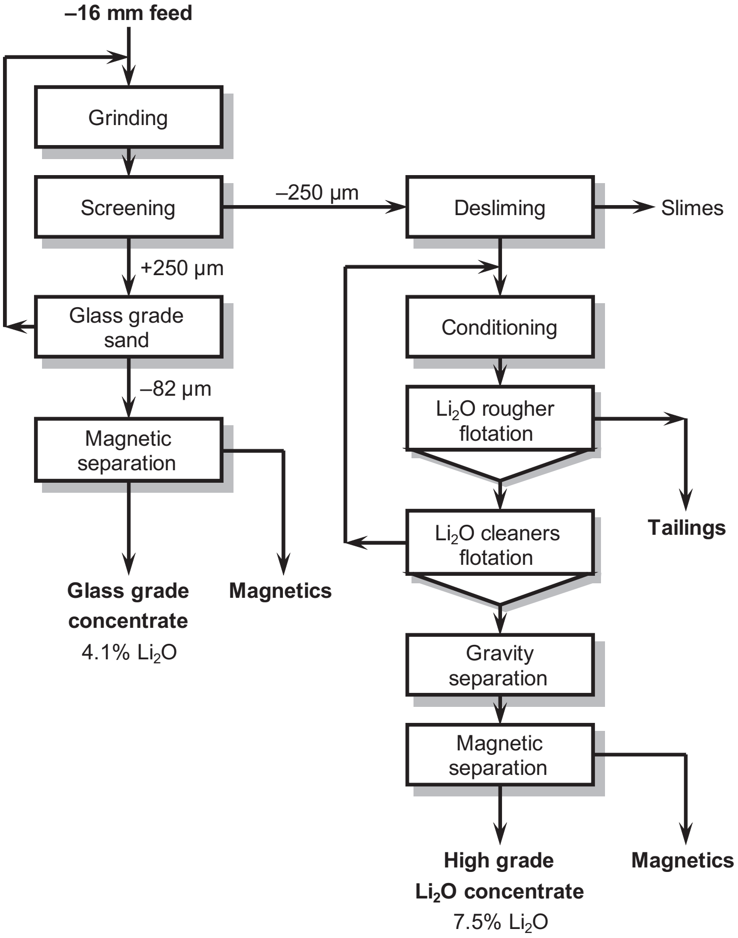

FIGURE 28.5

Greenbushes lithium plant flow sheet.

28.5.3 Spodumene flotation from King Mountain area, USA—Lithium Corporation of America

There are two producing plants, which treat a typical pegmatite ore from an open pit mine. One of the plants belongs to Lithium Corporation of America.

Typical ore grade that is processed in the plant is shown in Table 28.8.

The mill feed ore is crushed to 25 mm followed by rod mill, ball mill grinding. A fine grind is required to achieve liberation. The ball mill is operated in a closed circuit with cyclone about 300–400 g/t of NaOH is added to the mill. The ground ore is deslimed to remove 15 µm slimes. The deslimed sand is conditioned at 55% at natural pH with about 700 g/t of tall oil fatty acid. The conditioned pulp was floated at 30% solids followed by two cleaning stages. The plant flow sheet is shown in Figure 28.6.

The metallurgical results obtained are presented in Table 28.9.

Table 28.8 Typical Grade of King Mountain Spodumene Ore

Element	Assays %	Mineral Content %Wt
Li_2O	1.4–1.5	Spodumene = 15–25
Na_2O	1.2–3.8	Soda feldspar = 12–15
K_2O	2.2–2.7	Potash feldspar = 28–33
CaO	0.26–0.46	Quartz = 25.35
Al_2O_3	12.20–17.9	Muscovite and other = 5–15
Fe_2O_3	0.51–0.97	
LOI	0.50–0.75	

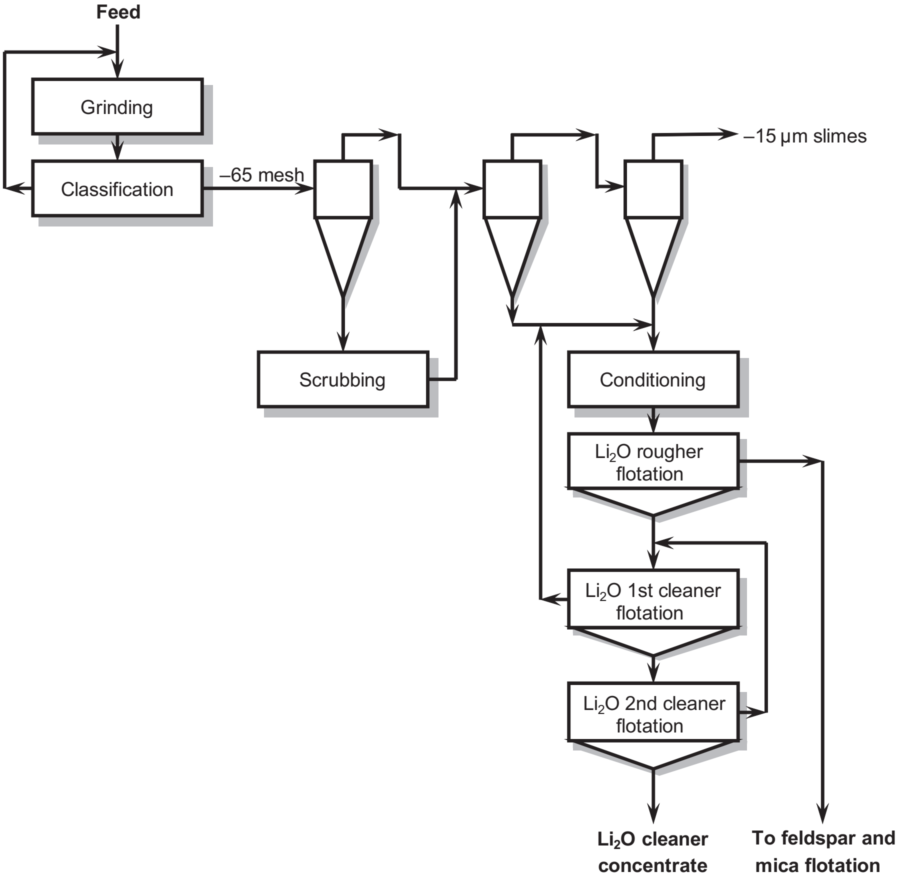

FIGURE 28.6

Flow sheet used for spodumene flotation at King Mountain, USA.

28.6 Chemical analyses of the spodumene concentrate from major world producers

The chemical analyses of the spodumene concentrate from major world producers are shown in Table 28.10.

High-grade spodumene concentrate is produced in Canada (Bernic Lake) and Australia (Greenbushes).

It should be noted that lithium is recovered from lithium rich brine. The major lithium rich brine is found in Chile (Atacama), Bolivia (Uyani), Argentina (Hombre Muerto), and USA (Silver Peak).

Table 28.9 Plant Metallurgical Results Obtained at King Mountain Ore

		Assays %		% Distribution
Product	**Wt. %**	**Li_2O**	**P_2O_5**	**Li_2O**
Spodumene Cl. concentrate	22.9	6.34	1.4	88.4
Spodumene tailing	69.7	0.12	–	5.1
Slimes	7.40	1.43	–	6.5
Feed	100.0	1.64	–	100.0

Table 28.10 Chemical Analyses of Spodumene Concentrate from Major World Producers

			Australia	
Element	**Canada**	**USA**	**Glass Grade**	**High Grade**
Li_2O %	7.25–7.30	6.3	5.01	7.5
Fe_2O_3 %	0.04–0.05	1.4	0.12	0.10
SiO_2 %	–	–	75.91	–
Al_2O_3 %	25–27	–	17.88	–
K_2O %	0.1–0.2	–	0.17	–
Na_2O %	0.15–0.20	–	0.09	–
P_2O_5 %	0.15–0.20	–	0.06	–
F %	0.01–0.02	–	–	–

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CHAPTER

Beneficiation of Florite Ores

29

CHAPTER OUTLINE

29.1 Introduction

The processing of fluorite ores especially of those that contain calcite minerals represents difficult problems due to the fact that the flotation properties of fluorite, calcite, and other gangue minerals are similar.

Fluorite (CaF_2) is an important source used in the production of hydrofluoric acid, manufacture of glass, aluminum industry, and as a flux in steel making.

Most fluorite ores have to be upgraded to various grades. For example fluorite concentrate with a grade of 98–99% CaF_2 is used for the production of hydrofluoric acid (acid grade). Metallurgical grade of fluorite ranges from 85% to 95% CaF_2.

The most commonly used beneficiation process is flotation where acid grade or metallurgical grade is produced depending on the ore type treated.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00004-X

Typically, in most cases fatty acid is used as a fluorite collector. However, most recently a new line to selective collectors was developed, especially for the beneficiation of complex ores.

The choice of a depressant system depends on the type of ore treated. The following depressants are usually employed in flotation of fluorite ores: (1) sodium silicate, (2) various tonic acid compounds, quebracho, (3) starches, and (4) dextrins.

Recently a number of new depressants have been developed. This includes (1) acidified silicate, (2) modified aluminum sulfate, and (3) various alginates.

Heating flotation feed in the presence of collectors to between 30 °C and 80 °C is practiced in some commercial operations. It has been reported that hot flotation of fluorite improves selectivity toward gangue minerals.

Apart from the flotation method, a heavy media separation is used, usually in combination with flotation.

29.2 Fluorite ore deposits

The main fluorite-containing mineral is fluorspar, CaF_2. In its pure form it contains 51.5% calcium and 48.9% fluorine, and has a specific gravity of 3.18. The hardness is about 4. Commonly it is glassy, colorless, white, or grayish.

It can be also purple, pink, blue, green, or yellow. Fluorspar belongs to a cubic system mineralogically and crystallizes into cubic shapes in vugs and cavities. In most of the ore types it appears in massive forms, with interlocking crystals.

Fluorspar occurs in a variety of geological environments and it is widespread throughout the world in North America, Asia, Europe, and Africa.

Mineable fluorspar deposits occur as bedded limestone, replacement deposits along fault zones, fissure-filling vein deposits, breccia fillings in limestones, dolomites, or various igneous rocks; replacement in carbonate rocks along contacts with acid igneous intrusives; replacement of igneous material in stockworks, dikes, and breccia pipes; residual deposits in clays resulting from weathering; and occurs as a recoverable gangue mineral in base and precious metal deposits.

Some vein deposits found in North America occur in fault fissures mainly in granite as crystals or massive crystalline veins. In addition, these deposits contain up to 10% barite.

The barite–fluorite deposits are vein deposits that are composed of a number of vein systems with a variable ratio of barite and fluorite. Fluorite in these deposits occurs in many varieties such green, purple, and colorless. Such deposits are found in Asia and Eastern Canada.

A quite unique deposit that contains fluorite is found in Western Canada. In these deposits fluorite occurs with celestite, quartz, feldspar base metals, sulfides, and rare earths. Most of the fluorite (i.e., 29% CaF_2) contains inclusions of celestite and bastnaesite.

29.3 Research and development in beneficiation of fluorite ores

29.3.1 Introduction

Over the past 30 years extensive research work was carried out on various fluorite containing ores, in which other alternative reagent schemes including collectors and depressant systems were examined. The ores that are most difficult to treat are carbonaceous ores as well as disseminated fluorite-silicate ores and ores that contain barite.

From the processing point of view, the flotation properties of fluorite ore are similar to those of gangue minerals present in the ore (i.e., calcite dolomite, borite); therefore application of selective reagent schemes is essential for production of high-grade fluorspar concentrate. Fluorspar ore varies widely in its amenability to concentration using flotation techniques or combinations of gravity and flotation. Based on minerals and gangue composition and amenability to concentration [1], the different ore types can be divided into the following groups.

1. *Siliceous nonalkaline* earth ores in granite or granodiorite rocks. These ores, common in US, South Africa, and Mexico are disseminated, and grinding to liberation is the main problem in treating this ore type.
2. *Siliceous ore* with alkaline earth, consisting mainly of limestone and calcite. These ores carry lead, zinc, and other sulfides. In beneficiation of these ores, sulfides are recovered ahead of fluorspar flotation.
3. *Baritic alkaline earth* siliceous ores with sulfides where sulfides were recovered first followed by fluorspar flotation and barite depression. Standard barite depressants are dextrin, starches, or chromates.
4. *Weathered alkaline earth* ores with mica and residues of sulfide oxidation. In beneficiation of these ores, mica is recovered first followed by fluoride flotation.

29.3.2 Summary of the research and development—depressants and modifiers

Research work in treatment of fluorspar ores dates back to 1940 [2], and is conducted nowadays. Literature on beneficiation of fluorspar ore is extensive and includes a new development, such as new collectors, modifiers, and depressants.

29.3.2.1 Acidified silicates

In treatment of carbonatite ore, studies were conducted using acidified silicates [3].

It has been demonstrated that acidified silicate has an activating effect on fluorite, while it improves selective depression of calcite. A degree of acidification plays an important role in production of acid grade fluorspar. Figure 29.1 shows the effect of the degree of acidification on fluorspar concentrate grade.

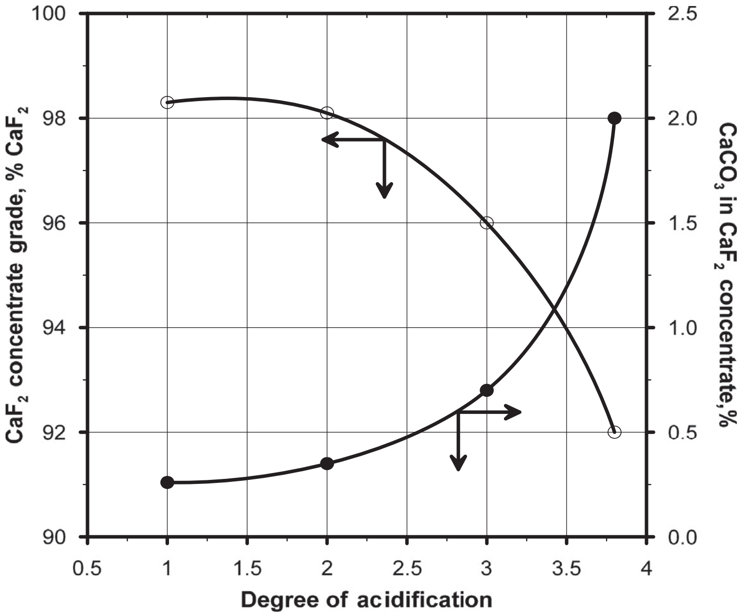


FIGURE 29.1

Effect of degree of silicate acidification on fluorspar flotation from carbonaceous gangue.

29.3.2.2 Modified copper sulfate

In the ores that contain phosphate, effective removal of phosphate [4] was achieved with the use of sodium chlorite (NaCl)-modified copper sulfate. The modified copper sulfate was prepared as follows:

First, 1% $CuSO_4$ solution and 2% NaCl is prepared separately in the same volume. At a solution temperature of 55 °C, the $CuSO_4$ solution is slowly added into the NaCl solution while slowly mixing to obtain CaCl-modified $CuSO_4$. The effect of modified $CuSO_4$ on phosphate removal from fluorite concentrate is illustrated in Figure 29.2.

29.3.2.3 Soda ash—quebracho system

Quebracho is used during fluorspar flotation as a selective depressant for calcite and limestone. Effectiveness of quebracho very much depends on the level and point of additions [5,6]. Higher addition of quebracho in the flotation improves fluorspar grade but reduces recovery. Table 29.1, shows the effect of levels of quebracho additions to the cleaners on fluorspar grade and recovery.

Different levels of quebracho were also examined during fluorspar rougher flotation using calcite dolomite ore. In these tests distilled oleic acid was used as a collector and Na_2CO_3 for pH control. With increasing levels of quebracho in the fluorspar rougher flotation stage, the concentrate grade increased while the fluorspar recovery was reduced (Figure 29.3). It has been determined by different researchers [7] that

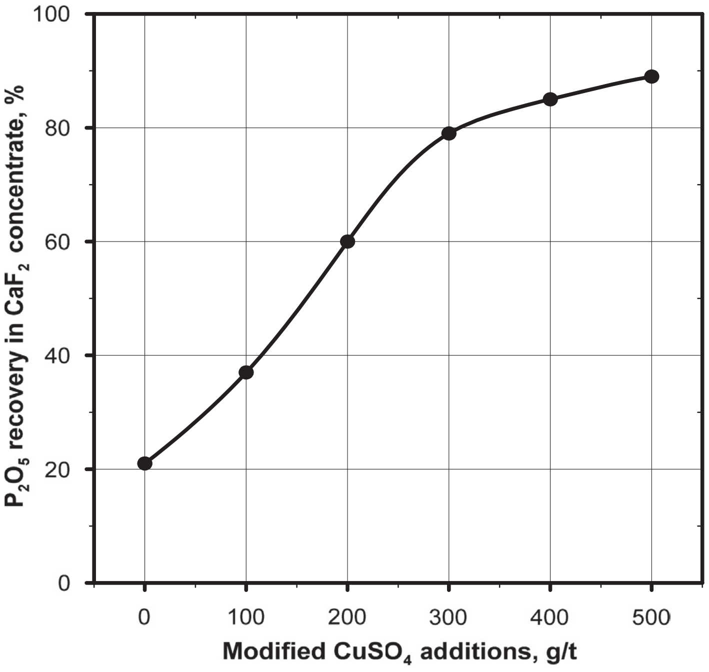


FIGURE 29.2

Effect of modified $CuSO_4$ on phosphate removal from fluorite concentrate.

Table 29.1 Effect of Level of Quebracho Additions to the Cleaners on Fluorspar Grade and Recovery

Quebracho Addition, g/t	**Concentrate Grade % CaF_2**	**Recovery % CaF_2**
0	87.25	81.3
300	98.13	18.2
150	88.25	83.2
250	92.00	80.1
280	95.55	40.7
440	96.86	13.4

equilibrium concentrations of both collector and quebracho are critical in selective separation of fluorspar and gangue mineral.

Therefore, the control of reagent regimes is quite important.

29.3.2.4 Starches and dextrins

In beneficiation of fluorspar, starches and dextrins are used as depressants for barite, micaceous minerals, sulfides, and to some calcite minerals. They are also good depressants for iron oxides.

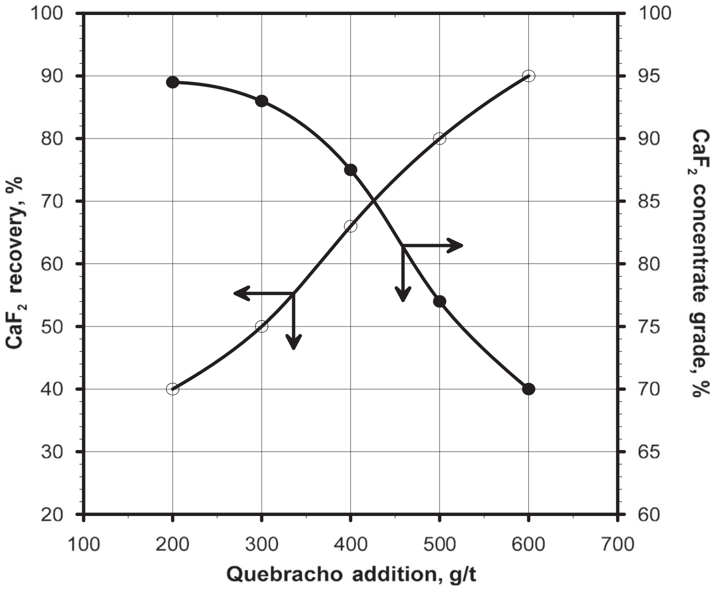


FIGURE 29.3

Effect of the level of quebracho additions on fluorspar rougher flotation.

Starches and/or dextrins are used in the treatment of most of the fluorspar ore types including siliceous ores, calcite silicate containing ores, barite containing ores, and sulfide containing ores. Types of starches and dextrins and their preparation method play an important role in their efficiency.

For example, causticized and boiled starches perform better than ordinary prepared starches. Branched dextrins are more efficient that standard unbranched dextrin. Studies were conducted on ores that contain calcite and quartz as main gangue minerals in which different starches and dextrins were examined [8]. The effects of different starches and dextrins on fluorspar flotation are presented in Table 29.2.

As can be seen from the results, the highest concentrate grade was achieved using either boiled caustic cornstarch or caustic potato starch.

29.3.2.5 Other depressants and modifiers

In beneficiation of fluorspar ore a number of secondary depressants and modifiers are used. Following is a brief description of the individual secondary depressants and modifiers:

1. Sodium fluorosilicate (Na_2SiF_6) is used in the treatment of barite containing fluorspar ore as a barite depressant. It also improves silica rejection.
2. Ligninsulfonate is sometimes used in place of quebracho in the treatment of barite containing ore; It improves barite depression.

Table 29.2 Effect of Different Starches and Dextrins on Fluorspar Flotation

Type of Starch or Dextrin Additions	g/t	Assays %			Recovery % CaF_2
		CaF_2	CaO	SiO_2	
Cornstarch	750	89	2.2	1.6	87
Caustic cornstarch	750	92	1.3	1.0	85
Caustic boiled cornstarch	750	97	1.1	0.6	83
Potato starch	750	90	0.8	1.5	88
Potato caustic starch	750	98	0.7	0.6	86
Yellow dextrin	400	93	1.2	0.8	88
Dextrin D82	400	94	1.0	0.9	85

Reagents: sodium silicate = 1100 g, pH = 9.2; quebracho = 250 g/t; oleic acid (Fal) = 200 g/t.

3. Tripolyphosphate $Na_4P_2O_7$ is used as a dispersant and also as an apatite depressant in the treatment of the ore with elevated slime content.
4. Depressant from A-3 series is modified sodium silicate with Na_2SO_3 and $Al_2(SO_3)_2$. This depressant is used in the treatment of refractory fluorspar ores. Depressant A3-2 consists of the following individual reagents:

$$Na_2SiO_3 = 70\,\%$$

$$Al_2(SO_3)_2 = 20\,\%$$

$$Na_2SO_3 = 10\,\%$$

   It has a depressing effect on dolomite, calcite silicates, and iron oxides.
5. Oxalic acid is used as a silicate depressant and also has a depressing effect on celestite.
6. Sodium and ammonium fluoride is used as a barite depressant and also as an activator when floating fluorspar with diamines, a cationic collector.

29.3.3 Summary of the research and development—fluorspar collectors

Typically, in the commercial operations, fatty acid collectors are used in fluorspar flotation. The performance of these collectors is well documented in the literature. Normally fatty acids are saponified in alkaline medium (i.e., NaOH). Most recently fatty acids are emulsified with the use of a surfactant plus fuel oil. Emulsified fatty acids performance is better than that of saponified fatty acid. The effect of emulsified and saponified fatty acid (i.e., oleic acid) is illustrated in Figure 29.4. The use of emulsified fatty acid with surfactant OP6 + fuel oil gave significantly better metallurgical results.

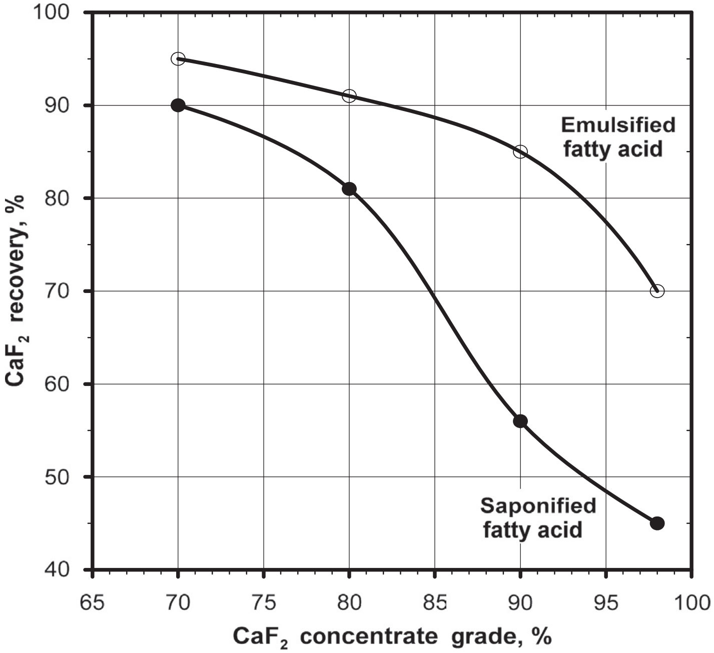


FIGURE 29.4

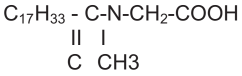
Effect of saponified and emulsified fatty acid on fluorspar flotation.

The type of fatty acid plays an important role in both selectivity and recovery of fluorspar [9,10]. Testwork with different fatty acids were performed on the ore that assayed 31.5% CaF_2. The results obtained are summarized in Table 29.3.

The best concentrate grade was obtained using a mixture of oleic/linolenic acid and with distilled oleic acid. Using tall oil fatty acid high CaF_2 recovery was achieved but with reduced concentrate grade.

In recent years, a new more selective collector was developed for the treatment of complex fluorspar ores. Some of these collectors and its effectiveness are summarized as follows:

- Oleyl sarcosine is examined on the ore that contains a relatively high amount of calcite. It has been reported that a remarkable improvement in the metallurgical result [11] were achieved with new fluorite collector oleyl sarcosine (*N*-oleoyl-*N*-methyl-amino carboxylic acid with the formula:



$$\begin{array}{l} C_{17}H_{33}\text{ - C-N-}CH_2\text{-COOH} \\ \qquad\quad\;\; \text{II} \;\; \text{I} \\ \qquad\quad\;\; \text{C} \;\; \text{CH3} \end{array}$$

This collector is known as Cordezin O. This collector is being used in Ilmenau concentrator (Germany).

Table 29.3 Effect of Different Types of Fatty Acids on Fluorspar Grade and Recovery

Fatty Acid Type	Assays %		Recovery % CaF_2
	CaF_2	SiO_2	
Oleic acid (Arizona FA3) 20% rozin acid	94.2	2.1	89.5
Oleic/linolenic acid (1:1) L-5	98.5	0.7	81.2
Distilled oleic acid (Arizona FA)	96.2	0.9	84.5
Fatty acid mixture (Soliflot 50A)	95.7	1.1	85.8
Tall oil fatty acid (D30LR) 30% rozin acid	90.2	3.3	89.3
Undistilled fatty acid (Hercules)	94.9	1.3	86.3

- Sodium naphthenate collector was examined using the fluorspar ore from the Fenglin plant (North China). The commercial name of the collector is GY-2 and is composed of 33.13% sodium naphthenate, 6.63% fatty acid, and 51% water. This collector is produced by mixing a by-product from the oil refinery with fatty acid. This collector comes with the carbon numbers between C_3 and C_6 carbons.
- In the study it was found that the number of carbons determines the fluorspar recovery. Figure 29.5 shows the effect of hydrocarbon number on fluorite recovery.
  The higher number of carbon improves CaF_2 recovery significantly.
- Collectors from AK-F Series were developed recently for beneficiation of refractory fluorspar ores that contain, in addition to calcite, clay, and iron oxides. Collector AK-F2 is composed of the following individual reagents [12].

$$\text{Oleic acid (FAl)} = 38\%$$

$$\text{Phosphate ester (AEP)} = 42\%$$

$$\text{Ethylene diamine} = 20\%$$

This collector was developed for beneficiation of the ore from India. The effectiveness of this collector is illustrated in Table 29.4 where comparative continuous locked cycle tests were performed using emulsified oleic acid and collector AK-F2.

A significant improvement in fluorspar metallurgical results was achieved with the use of the new collector as compared with the standard oleic acid collector.

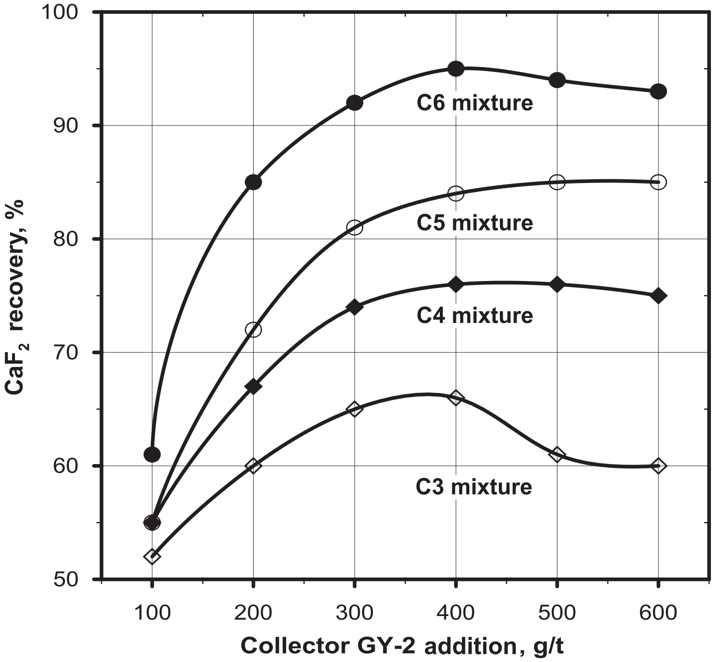


FIGURE 29.5

Effect of hydrocarbon number in the reagent GY-2 on fluorite recovery from Fenglin (China) ore.

29.3.4 Commercial treatment processes for beneficiation of various fluorspar containing ores

29.3.4.1 Siliceous monocline earth ores

These are disseminated ores and require relatively fine grinding to achieve liberation. Normally, grinding to about $K_{80} = 50\,\mu m$ is required to achieve liberation.

A typical flow sheet for beneficiation of this ore is presented in Figure 29.6.

Depending on the head grade, the flow sheet may include seven to nine cleaning stages. A typical reagent scheme used to treat this type of ore is shown in Table 29.5.

It has been demonstrated that the use of emulsified oleic acid with surfactant plus fuel oil improves selectivity and fluorspar recovery.

For the ores that do not have calcite, little or no quebracho is used. In some cases quebracho may be replaced with ligninsulfonate.

In case of coarse-grained, high-grade fluorspar ore, such as Minere de los Cuevas (Mexico), which assays 75% CaF_2 in the head only Quebracho was used to produce acid grade CaF_2 concentrate.

Table 29.4 Effect of Collector AK-F2 on Fluorspar Flotation From India

				Assays %			
Test No.	**Collector Type**	**Product**	**Wt %**	**CaF_2**	**SiO_2**	**CaO**	**Recovery % CaF_2**
78	AK-F2 = 800 g/t	CaF_2 rough Cl concentrate	12.47	97.50	0.6	0.4	54.4
		CaF_2 scavenger Cl concentrate	8.40	83.35	1.2	2.2	31.3
		CaF_2 flot. tail	67.14	0.87	–	–	2.6
		Slimes	11.99	21.81	–	–	11.7
		Feed	100.0	22.36	–	–	100.0
81	Oleic acid = 900 g/t	CaF_2 rough Cl concentrate	9.70	92.20	3.3	2.8	40.6
		CaF_2 scavenger Cl concentrate	5.1	78.30	6.9	5.6	20.7
		CaF_2 flot. tail	72.4	8.52	–	–	27.0
		Slimes	11.99	21.81	–	–	11.7
		Feed	100.00	22.36	–	–	100.0

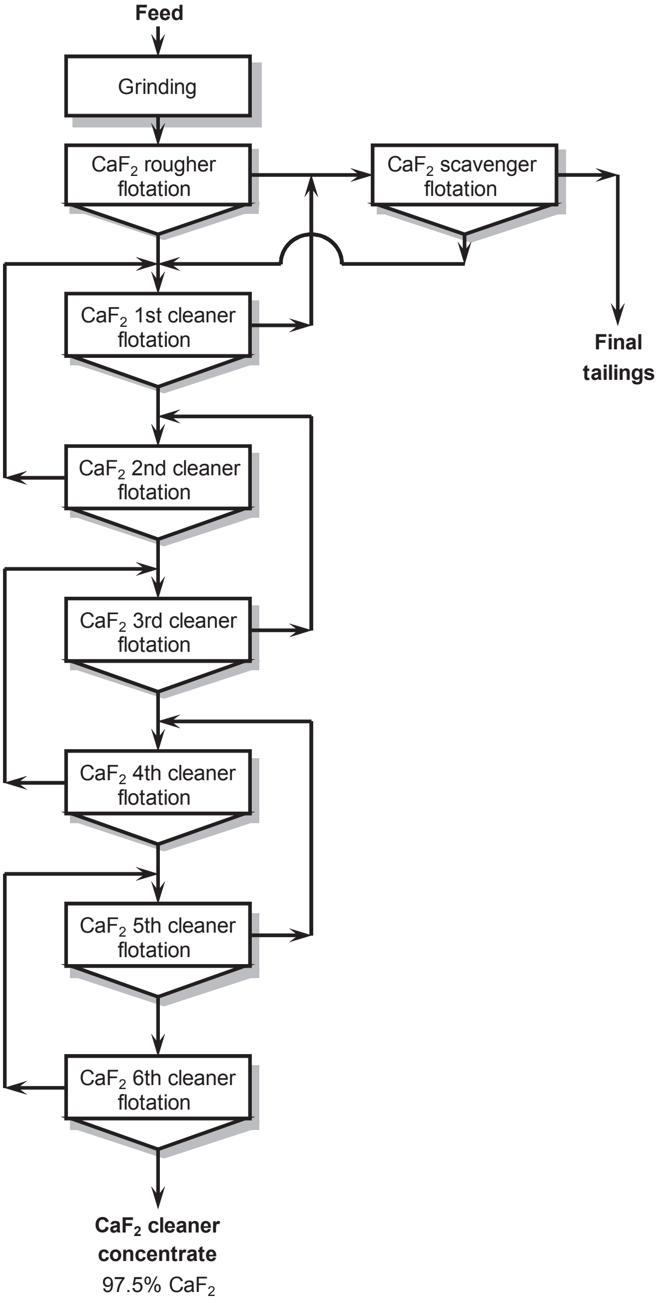


FIGURE 29.6

Flow sheet used in beneficiation of siliceous monocline earth ore.

Table 29.5 Typical Reagent Scheme Used in the Treatment of Siliceous Monocline Earth Ore

Reagents	Additions, g/t		pH
	Condition of Rougher	Cleaners	
Depressants and Modifiers			
Na_2CO_3	800–1200	300	9.0
Na_2SiO_3 (type N)	700–900	400–700	
Quebracho	0–400	300–600	
Caustic starch[1]	0–600	400–800	
Collectors			
Oleic acid (saponified)[2]	200–350	50–300	9.0
Fuel oil	Optional	Optional	

[1] *Optional.*
[2] *Saponified with surfactant.*

Table 29.6 Typical Reagent Scheme Used in Treatment of Mixed Siliceous Calcite Ores

Reagents	Additions, g/t		pH
	Grind + Rough	Cleaners	
Soda ash (Na_2CO_3)	To pH	–	9.0–10.5
Sodium silicate (Na_2SiO_3)	600–1000	200–300	
Tannic acid	200–300	50–100	
Caustic starch	200–300	50–150	
Emulsified oleic acid	150–300	–	

29.3.4.2 *Mixed siliceous calcite fluorspar ores*

These ores are medium- to fine-grained ore where a portion of fluorspar is associated with silicates. Some of these ores are disseminated and require a relatively fine grind to achieve liberation (i.e., 28 μm–44 μm).

The reagent scheme used to treat this ore type is shown in Table 29.6. The typical flow sheet used for treatment of this ore type is shown in Figure 29.7.

Such ore types are found in Norway, China, and Canada.

The most effective starches are cornstarch and tapioca starch. In some cases, tonic acid is replaced with quebracho.

Tannic acid usually does not depress CaF_2 at higher additions as does quebracho.

Some operations in Mexico and South Africa produces acid grade fluorspar assaying 97.5–98% CaF_2 with less than 1% SiO_2.

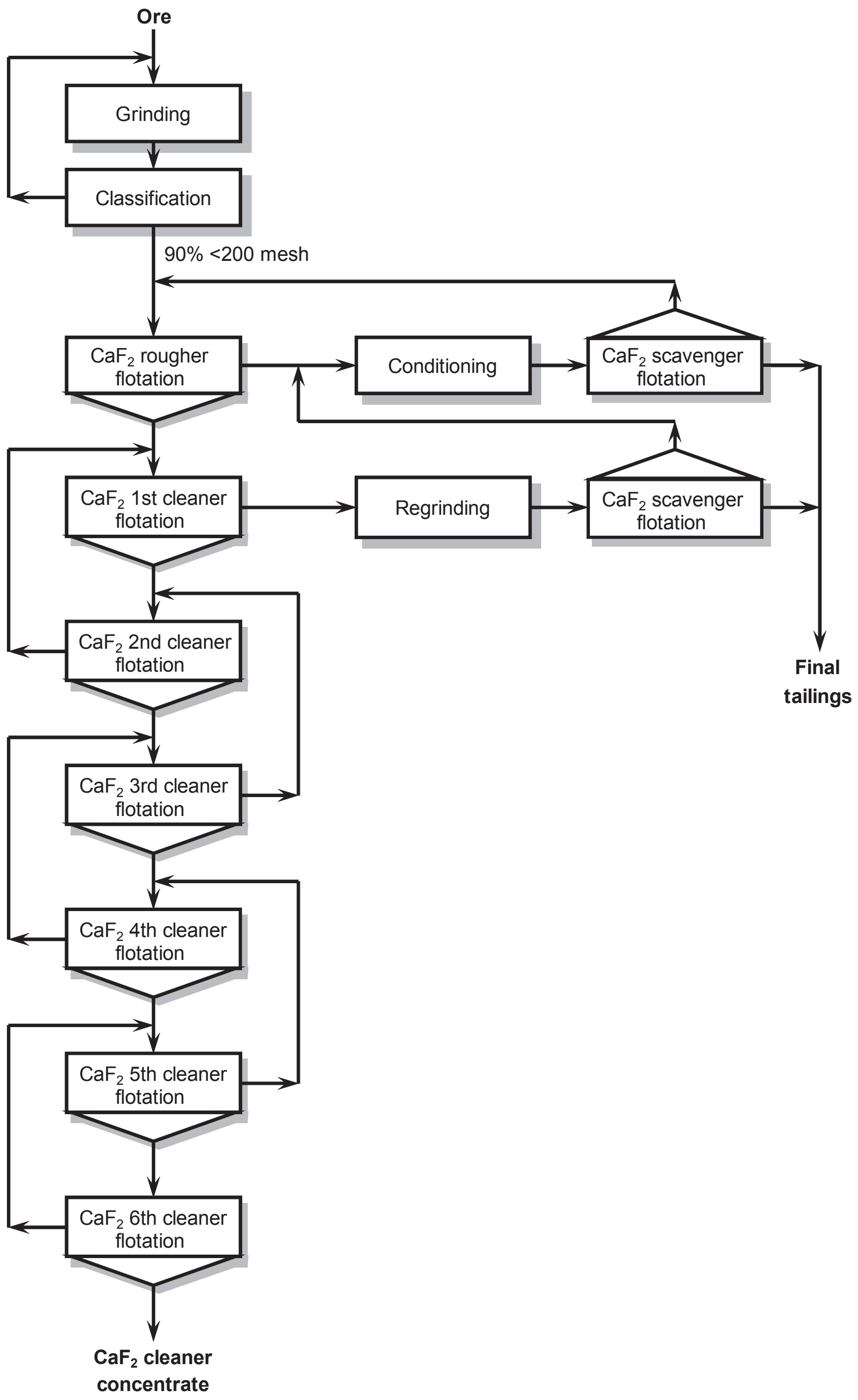


FIGURE 29.7

Flow sheet used for treatment of mixed siliceous calcite ore.

29.3.4.3 Treatment of barite–fluorspar ores

The barite–fluorspar ores are sometimes associated with base metals (i.e., lead, zinc). These ores are found in Russia, Canada, and China. These ores may also contain significant quantities of REO (i.e., bastnaesite). These ore types are usually coarse grained and liberation occurs between 65 and 100 mesh.

In treatment of these ores sequential barite flotation is followed by fluorspar flotation. The reagent schemes used in the sequential barite fluorspar flotation is described as follows.

29.3.4.3.1 Barite flotation

Major CaF_2 depressant during barite flotation is citric acid. A number of barite collectors can be used including: (1) alkyl sulfate (Flotinor S72), (2) succinamate, (R845), and (3) petroleum sulfonate (R825 or R827). The most selective collector is Flotinor S-72 or a mixture of the above three collectors.

29.3.4.3.2 Fluorspar flotation

The reagent schedule is more or less standard where sodium silicate quebracho and starch are the main depressants. The selective flotation of CaF_2 is determined by the type of fatty acid used. Fatty acid of tallow origin with 70–80% oleic content and oleic linoleic acid with 56% oleic acid, 40% linoleic of vegetable origin are the most selective CaF_2 collectors.

A typical reagent scheme used during sequential barite–fluorspar flotation is shown in Table 29.7.

The fluorspar flotation feed is heated to 60 °C but to 70 °C while conditioning with collectors.

The flow sheet used in sequential barite fluorspar flotation is shown in Figure 29.8.

Other collectors suitable for barite flotation are petroleum sulfonate and succinamates. In a number of operations, barite concentrate grade assaying 95–98% $BaSO_4$ at 90% recovery has been achieved.

Table 29.7 Reagent Scheme Used in the Sequential Barite Fluorspar Flotation

	Reagent Additions, g/t		**pH**	
Reagent	**Barite Circuit**	**Fluorspar Circuit**	**$BaSO_4$**	**CaF_2**
Modifiers and Depressants				
Sodium silicate	300–800	200–300	8.0-8.5	9.0–9.5
Citric acid	200–400	–		
Sodium carbonate	To pH	To pH		
Quebracho	–	150–300		
Collectors				
Flotinor S-72	600–900	–		
Oleic acid (emulsified)	–	120–200		

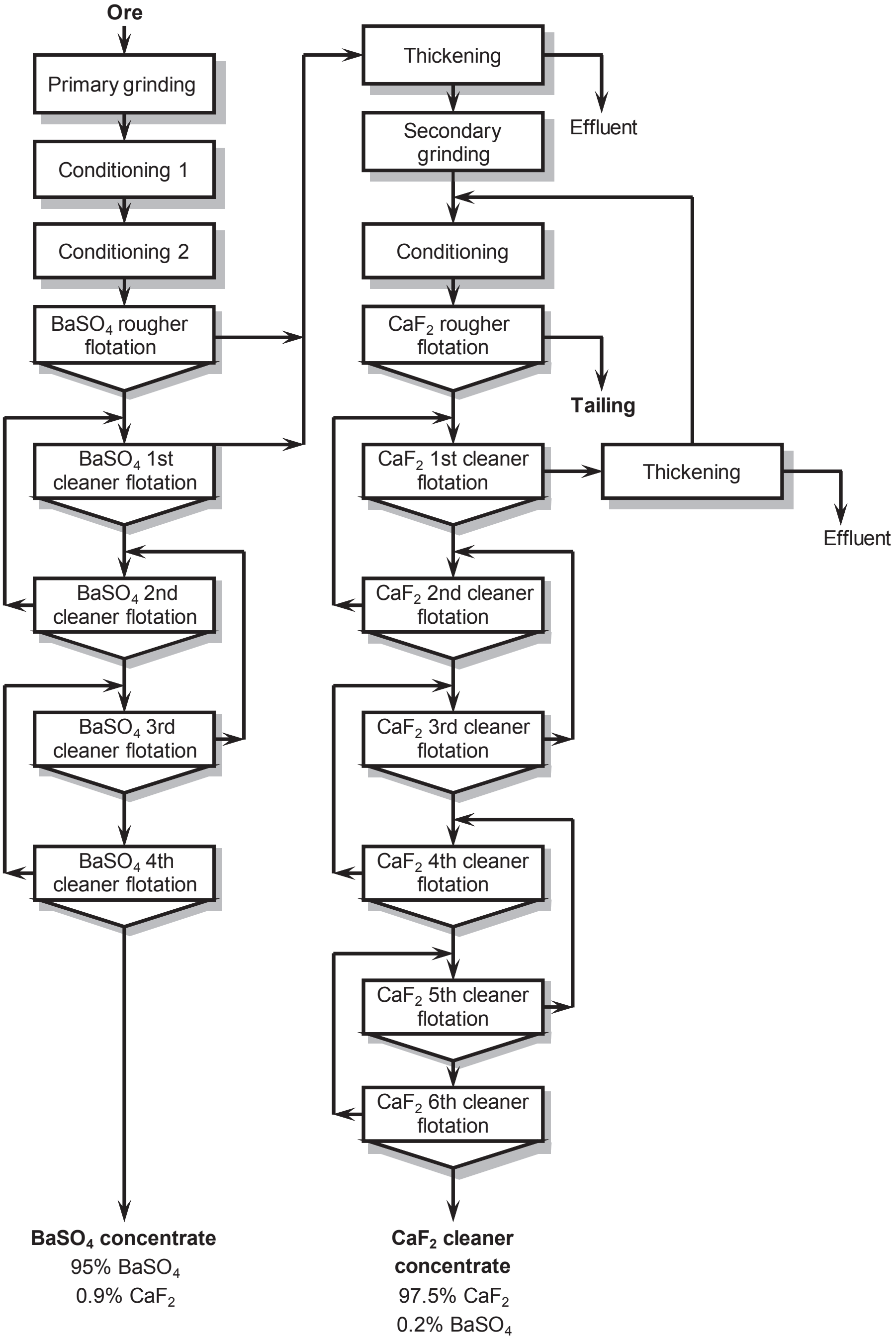


FIGURE 29.8

Flow sheet used in sequential barite–fluorspar flotation.

When most of the barite is recovered in the barite circuit, a fluorspar concentrate grade of 97.5% CaF_2 at 85% recovery is achieved.

29.3.4.4 Treatment of mixed sulfide fluorspar ores

A typical example of the mixed sulfide fluorspar ore is Eagle Pass operated by Reynolds Mining Corporation (Texas, USA). Primary grinding fineness of ore ranges from 65% to 85% minus 200 mesh. The regrind of the scavenger concentrate to achieve liberation is also practiced.

The typical flow sheet used in the treatment of mixed sulfide fluorspar ore is shown in Figure 29.9.

Because the first cleaner tailing contains most of the middlings, the tailing is reground before either retreatment or returning to the circuit. The order of flotation of mixed sulfide fluorspar ores is as follows:

29.3.4.4.1 Galena pyrite flotation

Galena pyrite is floated with xanthate zinc sulfate and cyanide is sometimes used to depress sphalerite.

29.3.4.4.2 Zinc flotation

Zinc is floated with aeroflot collector R211 after activation with $CuSO_4$ at a natural pH of 8.0–8.5. Zinc tailing is then subjected to fluorspar flotation.

29.3.4.4.3 Fluorspar flotation

The zinc tailing is thickened to 60% solids conditioned while steam heating to 50 °C followed by CaF_2 flotation and upgrading. The most selective collector is a fatty acid of vegetable origin consisting of 40% linoleic, 55% oleic, and 1–3% resin acid.

The typical depressant system used is: Quebracho sodium silicate and caustic starch.

Quebracho is the selective depressant for calcite and limestone. Sodium silicate is the depressant for quartz and other silicate minerals and caustic starch is used for depression of barite, micaceous minerals, and sulfides. The raw extract of quebracho is treated with sodium bisulfite to make it water soluble. Effectiveness of quebracho as a depressant is dependent on the preparation method.

The typical reagent scheme used in the treatment of mixed sulfides fluorspar ore is shown in Table 29.8.

29.3.5 Major producers and chemical composition of commercial acid grade fluorspar

The major producing countries of chemical grade fluorspar are: Italy, Mexico, Morocco, South Africa, Spain, U.K., USA, and China. The concentrates produced assayed over 97% CaF where the highest grade is produced by Morocco.

Table 29.9 shows chemical compositions of CaF_2 produced by various producers.

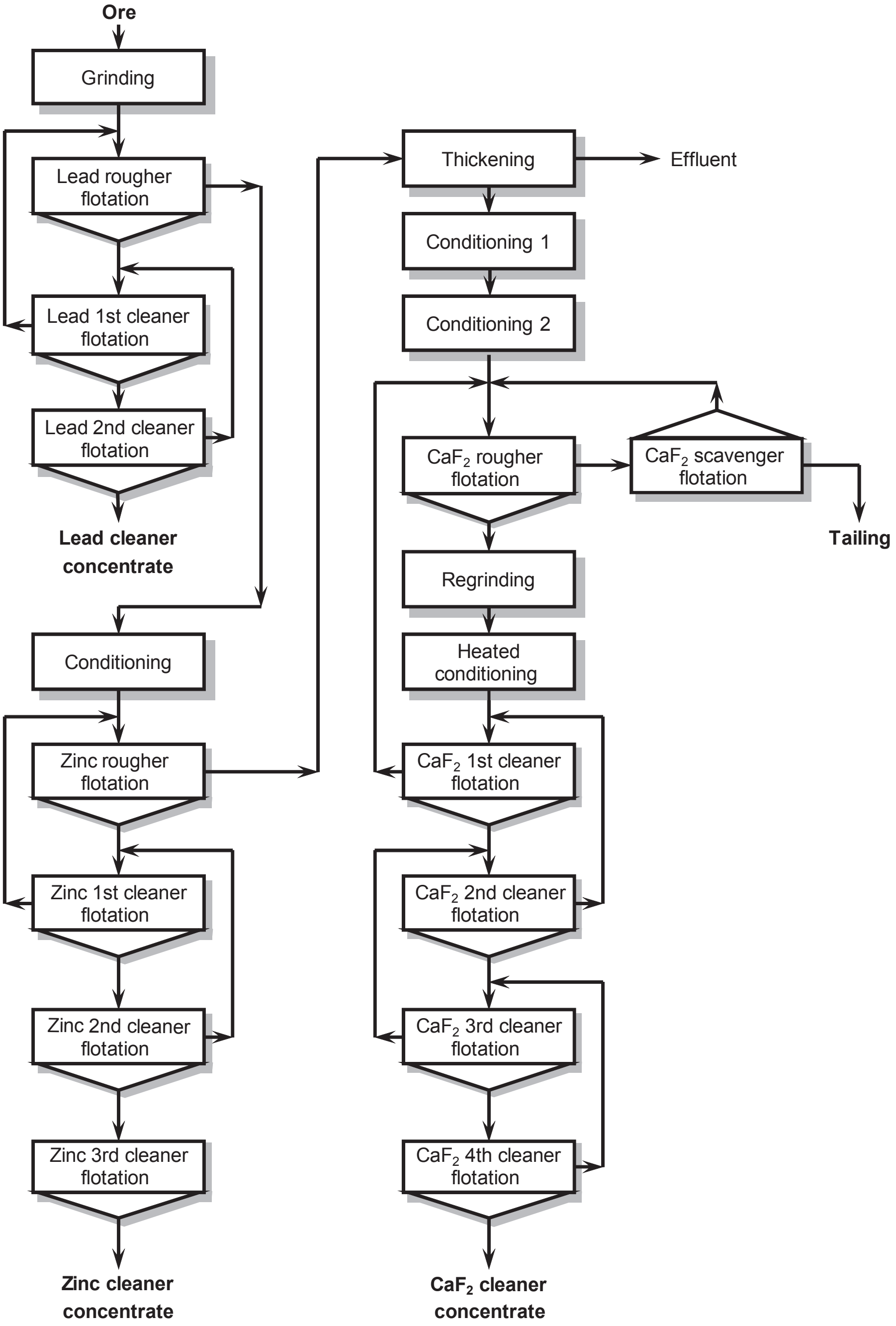


FIGURE 29.9

Flow sheet used in the treatment of mixed sulfide fluorspar ores.

Table 29.8 Reagent Scheme Used in Flotation of Mixed Sulfide Fluorspar Ore

Reagent	Additions, g/t		
	Lead Pyrite Circuit	Zinc Circuit	Fluorspar Circuit
Sodium ethyl. xanthate	20–40	–	–
Methyl Isobutyl Carbanol (MIBC) frother	5–10	5–10	–
Zinc sulfate	300–500	–	–
Copper sulfate	–	200–400	–
Aeroflot 211	–	30–60	–
Soda ash	–	–	800–1200
Sodium silicate	–	–	600–800
Quebracho	–	–	600–800
Caustic starch	–	–	200–400
Fatty acid emulsifier	–	–	200–300

Table 29.9 Chemical Compositions of Commercial Acid–Grade Fluorspar

Element	Assays						
	Italy	Mexico	South Africa	Morocco	Spain	UK	USA
CaF_2 (%)	97.58	97.52	97.58	98.23	97.56	97.60	97.80
SiO_2 (%)	0.75	0.89	0.84	0.57	0.98	0.40	0.62
$CaCO_3$ (%)	0.68	0.79	0.30	0.66	0.75	1.30	1.33
Total S (%R)	0.14	0.036	0.004	0.022	–	–	–
Sulfide S (%)	0.015	0.013	0.002	0.014	0.013	–	0.028
Arsenic (ppm)	10	300	3.0	1.0	10	2	1.0
P_2O_5 (ppm)	160	540	320	50	180	0.5	0.0
NaCl (ppm)	140	40	170	200	180	–	–

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CHAPTER

Wollastonite

30

CHAPTER OUTLINE

30.1 Introduction

Although the first production of wollastonite dated back to 1935 in California, USA, there has been very little development testwork especially in flotation done over the years. In a number of operating plants beneficiation is performed using: (1) sorting and (2) magnetic separation. In a few plants reverse flotation of gangue minerals from wollastonite is practiced.

Because gangue minerals present in the wollastonite containing ore have similar flotation properties, the beneficiation of the ore using flotation method is relatively complex and rather difficult.

In this chapter, the research and development as well as the beneficiation processes are described.

30.2 Wollastonite minerals and deposits

Wollastonite is a mineral form of calcium metasilicate ($CaSiO_3$). It has a theoretical composition of 48.3% CaO and 51.7% SiO_2, when it is pure. However, in nature the calcium component is often substituted by iron magnesium or manganese.

The commonly associated mineral in the ore are:

Diopside = $CaMgSiO_6$
Tremolite = $Ca(MgFe)_5Si_8O_{22}(OH_2)$

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00005-1

Idocrase = $Ca_{10}Al_4(MgFe)_2(Si_2O_7)(SiO_4)_5(OH)_4$
Grossulat Garnet = $Ca_3Al_{2(}SiO_4)_3$ and
Andradite Garnet = $Ca_3Fe(SiO_4)_3$

Wollastonite is found in silicated metalimestone that has been affected by regional metamorphism or local igneous activity. Deposits of sufficient size and purity are rare.

In a pure state, wollastonite has the following properties:

Hardness (Mohs scale) = 4.5–5.0
Specific gravity (g/cc) = 2.8–3.09
Moisture content = 4.0 Max
Retroactive index = 1.616–1.631
Crystal system = monoclinic
Common form = masses of aggregates of bladed or needle-like crystals
Luster = vitreous, transparent to translucent.

Although the mineral is white when being pure, it is often colored, gray, or brown due to impurities and it is the nature of these impurities, which determine whether the mineral is economically exploitable.

Because of the complex nature of the ore, the production of wollastonite is limited.

30.3 Beneficiation of wollastonite ore

There are three main methods by which wollastonite is concentrated, these include:

1. Mechanical sorting;
2. Magnetic separation dry or wet;
3. Flotation—a/u? Combination of physical separation and flotation. In some cases, combinations of magnetic separation and flotation are used.

30.3.1 Mechanical sorting

The mechanical sorting of the ore is applicable if in case wollastonite is present in the ore in the form of large crystals. The wollastonite from the host rock is separated by hand cobbing, the product being marketed in lump form.

Hand cobbing was practiced in the early 1970s in Finland and some operations in China and Romania.

30.3.2 Dry or wet magnetic separation

Wet magnetic separation [1] has been evaluated on several deposits from New York, US. Using a pilot plant, finely ground unsized wollastonite ore is diluted in water and passed through a high intensity oscillating wet magnetic separator of special design and in a single pass over 90% wollastonite exhibiting crystal purity of 99% was obtained. The product was then ground and sized to obtain products of different sizes.

The ore used in this study was of skarn origin containing 55–65% wollastonite. Wollastonite was well crystallized. The gangue minerals were diopside and garnet comprising of a mixture of androdite, grossularite, and salite.

Dry magnetic separation is used on the ore that contains mainly garnet. It is also used in combination with gravity. A typical flow sheet used in ore treatment using dry magnetic separation is shown in Figure 30.1.

In this case the ore is crushed using roll crushers to 16 mesh nominal size. The ore is screened into three size fractions, followed by treatment on air tables and high-intensity magnetic separation. Using this method, a high-grade wollastonite concentrate was produced with aspect ratio of up to 15 (aspect ratio = diameter by length of particles). The screens' opening and number of size fractions depend on the type of ore treated.

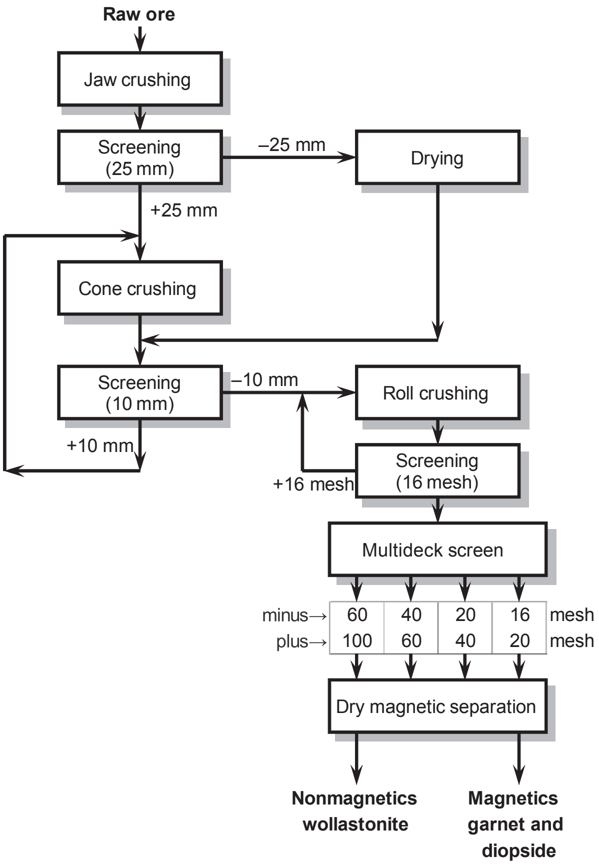

FIGURE 30.1

General flow sheet used for recovery of wollastonite using dry magnetic separation.

30.3.3 Flotation methods research and development

Because wollastonite forms needle-like crystals selective flotation of wollastonite from gangue minerals is rather difficult. Reverse gangue flotation or bulk flotation followed by separation of wollastonite from gangue minerals is often practiced. For example, in the ores that contain calcite minerals, calcite is first floated using sulfate soap followed by gangue flotation (i.e., silica, feldspar) using amine flotation.

In the Romania Research Institute, development work was carried out on iron containing ore [2,3] and the ore that contained garnet diopside and epidote. In the case of iron containing ore, the ground ore was subjected to single-stage magnetic separation followed by reverse gangue flotation using sulfate soap collector. Using this method a wollastonite with 95% purity at 86% recovery was achieved.

The ore that contains garnet diopside and epidote was treated by using reverse gangue flotation.

The ground ore is conditioned with sulfuric acid to pH 6–6.5 and the gangue minerals are floated using sulfate soap collector (i.e., sodium dodecyl sulfate).

The ore that contains mostly calcite with some quartz and iron silicate is processed as follows.

The ground ore is first conditioned with fatty acid followed by calcite flotation. The calcite tailing was deslimed followed by silicate flotation using a mixture of anionic and cationic collector [4].

Some research work was carried out by the Russian Institute SAIGIMS. The ore that contains about 70% wollastonite, 20% mixture of feldspar, and 7% pyroxene with minor amounts of quartz and calcite was treated using reverse gangue flotation. First calcite was floated under alkaline conditions with tallow soap or saponified naphthenic acid collector.

The calcite tailing was treated with sulfuric acid and feldspar was floated using collector ANP-14 (amine).

In the final stage, pyroxenes were removed using a soap collector together with 600 g/t lead nitrate as an activator. Using this method a wollastonite concentrate assaying 92% wollastonite at 81% recovery was produced. The flow sheet using reverse flotation process is shown in Figure 30.2.

Research and development work on Canadian ore that contains feldspar, quartz, and diopside was conducted using air classification where a portion of fine gangue was recovered followed by bulk wollastonite–diopside flotation and wollastonite–diopside separation. The flow sheet used in this separation is shown in Figure 30.3. In preparation of the ore, the crushed ore is dried and ground in a roll crusher. The fines of about 10-mesh size are treated in an air classifier where a portion of coarse fraction is returned to the roll crusher. The fines were flotation feed. Initially, wollastonite and diopside were floated using collector SM15 (phosphoric acid ester) in alkaline pH, the concentrate was cleaned twice, followed by conditioning with sulfuric acid to pH 5.5, and diopside was floated without collector additions.

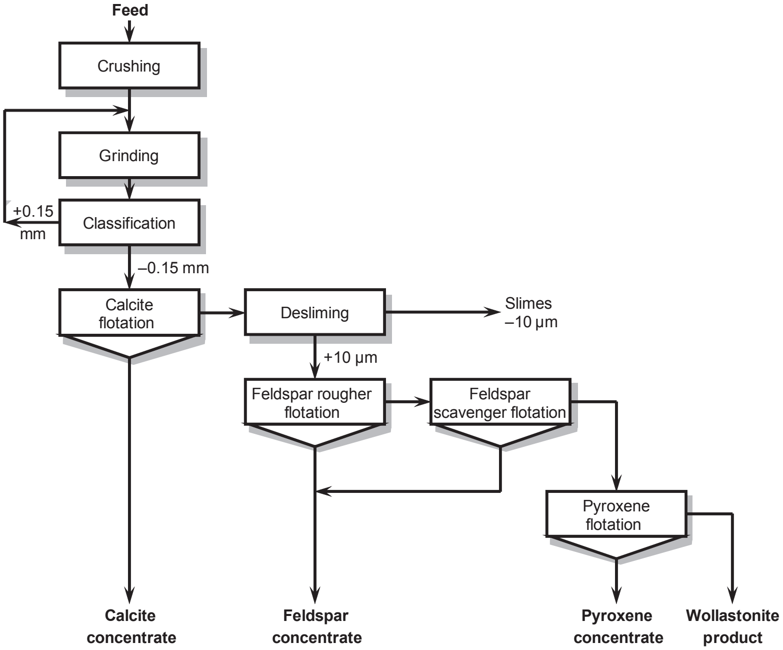

FIGURE 30.2

Flow sheet used for reverse gangue flotation.

30.3.4 New process for beneficiation of complex wollastonite ore

During several years of extensive studies, a new process has [5,6] been developed for the beneficiation of wollastonite ore. Most of the research work was conducted on St. Lawrence wollastonite ore located near Kingston, Ontario, Canada. Confirmation testwork was performed on an ore in Finland.

30.3.4.1 Mineralogy of the ore

Based on the mineralogical data, the ore is composed of wollastonite (44%) diopside (31%), feldspar (17%), and quartz (6%) as a major mineral. Small quantities of calcite, titanate, and sulfides were also present in the ore. Model abundance and liberation profile is presented in Table 30.1.

30.3.4.2 Processing characteristics

The gangue minerals contained in the ore have similar flotation properties as wollastonite and therefore selective flotation of wollastonite from the gangue minerals is rather difficult. Another problem related to selective flotation of wollastonite is the shape of wollastonite crystals. Wollastonite crystals are needle-like at an aspect ratio above 8, so attachment of wollastonite on the air bubbles is nonselective.

The new studies were directed toward wollastonite depression and the gangue flotation method using specific collector blends. Depressants examined, were mainly

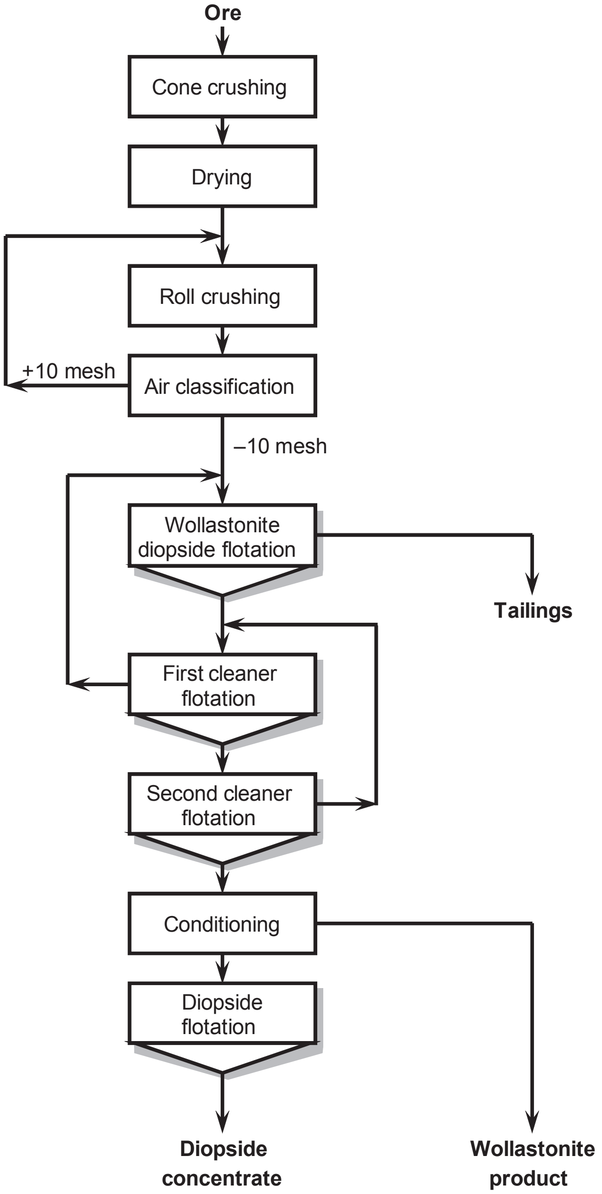

FIGURE 30.3

Double stage flow sheet with bulk flotation followed by wollastonite diopside separation.

organic acids such as, oxalic acid, lactic acid, citric acid, and acetic acid. The effect of different organic acids on wollastonite depression during reverse gangue flotation is illustrated in Figure 30.4. Oxalic acid, citric acid, and lactic acid had little or no depressing effect of wollastonite during reverse gangue flotation.

Table 30.1 Model Abundance and Liberation Profile of St. Lawrence Wollastonite

Mineral	Wt %	Size	Liberation	Textural Comments
Wollastonite	44	20–1000 μm	99%	Common forms of subhedral particles in habit, ranges in habit from prismatic to columnar to acicular and platy It is typically fresh with scarce calcite alteration and prehnite alteration
Diopside	31	50–1000 μm	99%	Subhedral, angular, tabular, and stubby crystals Variably replaced by prehnite, calcite, hosts minor inclusions of other diopside grains
Feldspars	17	50–450 μm	99%	Feldspars are mainly microcline, less albite, angular grains
Quartz	6	<20–350 μm	99%	Anhedral, angular grains, liberated, less albite, angular grains
Calcite	1	<20–400 μm	99%	Minor anhedral and angular grains, typically liberated, and alteration to wollastonite
Titanate	0.2	<150 μm	99%	Minor anhedral, liberated grains
Garnet	<0.1	<100 μm	99%	Minor anhedral, liberated grains
Sulfides	0.5	<10–200 μm	99%	Anhedral pyrrhotite, liberated
Fe-oxy-hydroxides	<0.1	<100 μm	99%	Anhedral aggregates, occurring as free grains or scarce stains on gangue minerals

Excellent wollastonite depression during gangue flotation was achieved using acetic acid. Other major parameters that effect production of high-grade wollastonite include (1) type of collector, (2) flotation pH, and flow sheet configuration.

Collectors RW9 and WK1 were the final collectors developed for reverse gangue flotation. Collector RW9 is composed of a mixture of petroleum sulfonate (R855) and alkyl sulfosuccinate (SM35) and is used for feldspar flotation in Stage 1.

Collector WK1 is a mixture of sodium alkyl sulfate (Flotinor AT), secondary amine (armoflote), and sodium oleate modified with surfactant. This collector is used for diopside and silica flotation.

Flotation pH between 6 and 6.2 gave the best wollastonite metallurgical results. Figure 30.5 shows the effect of pH on the wollastonite metallurgical results.

This flow sheet and reagent produced high-grade wollastonite at over 80% recovery. Metallurgical results obtained in continuous operation are presented in Table 30.2.

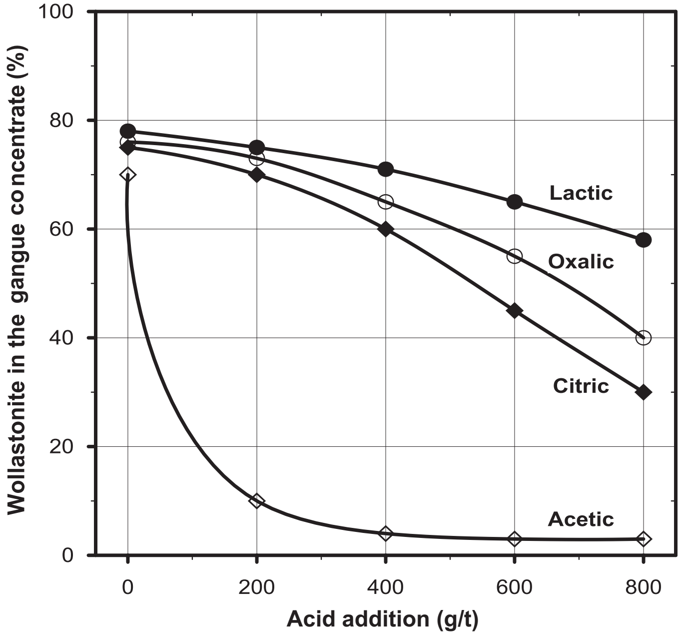

FIGURE 30.4

Effect of different organic acids on reverse wollastonite flotation.

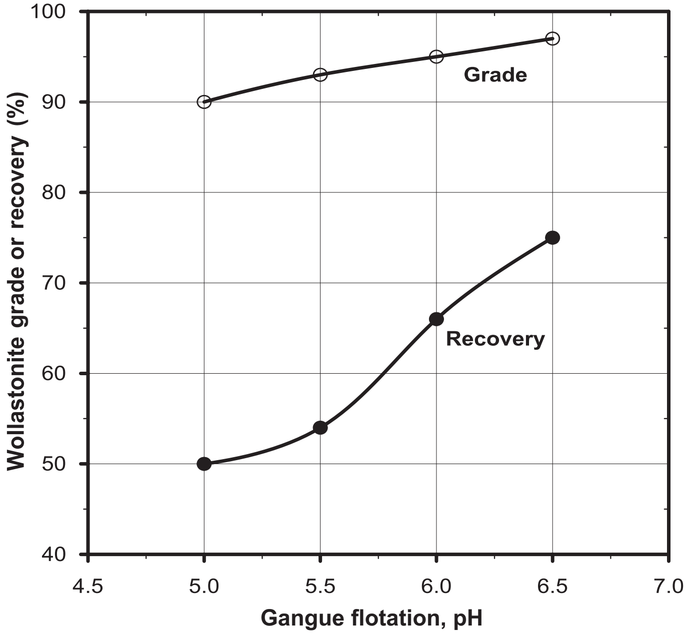

FIGURE 30.5

Effect of pH on wollastonite grade and recovery.

Table 30.2 Metallurgical Results Obtained in a Continuous Test

		Assays %						% Wollastonite
Product	**Wt %**	**SiO_2**	**CaO**	**Al_2O_3**	**MgO**	**Fe_2O_3**	**$CaSiO_2$**	**Distribution**
Wollastonite concentrate	43.53	51.9	47.3	0.015	0.023	0.059	97.0	81.0
Feldspar + diopside concentrate	54.97	56.55	23.14	3.13	9.24	1.75	17.16	18.1
Slimes	1.50	58.0	33.10	1.25	3.30	1.50	31.0	0.9
Feed	100.00	54.55	33.82	1.75	5.14	1.01	52.10	100.0

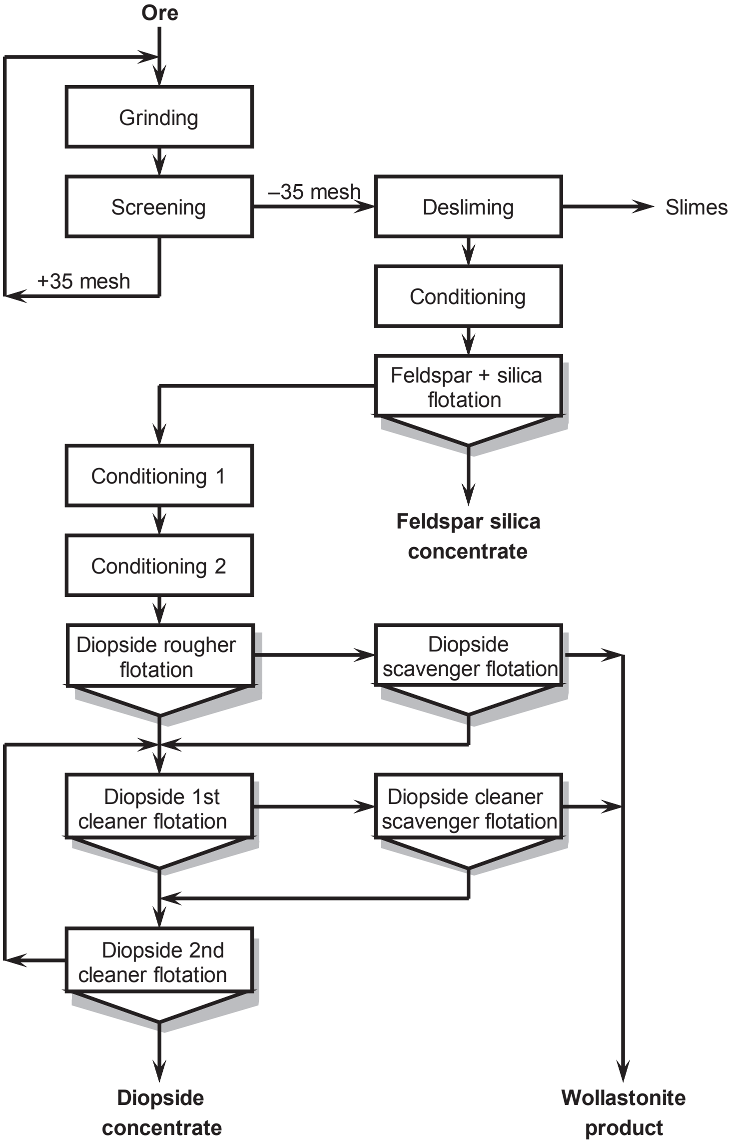

FIGURE 30.6

Two stage reverse flow sheet used in beneficiation of wollastonite ore.

The final flow sheet developed for beneficiation of wollastonite using reverse flotation involves grinding the ore to 35 mesh nominal size followed by desliming. The sand fraction is subjected to two-stage flotation. Initially feldspar and silica were floated using collector RW9, followed by diopside flotation using collector WK1. The final flow sheet is presented in Figure 30.6.

Table 30.3 Chemical Analyses of the Concentrate Produced on Various Ore Types

Element		**Assays**		
		Ore Type 1	**Ore Type 2**	**Ore Type 3**
Silica (SiO_2)	%	52.0	51.7	52.1
Calcium (CaO)	%	47.3	47.4	47.1
Alumina (Al_2O_3)	%	0.029	0.015	0.011
Iron (Fe_2O_3)	%	0.077	0.060	0.072
Magnesia (MgO)	%	0.25	0.022	0.06
Sodium (Na_2O)	%	0.11	0.05	<0.05
Potassium (K_2O)	%	<0.01	<0.01	<0.01
Titanium (TiO_2)	%	<0.01	0.005	<0.01
Phosphorus (P_2O_5)	%	<0.01	<0.01	<0.01
Manganese (MnO)	%	0.033	0.032	0.028
Chromium (Cr_2O_3)	%	<0.01	<0.01	<0.01
Vanadium (V_2O_5)	%	<0.01	<0.01	<0.01
Loss of ignition (LOI)	%	0.15	0.14	0.19
Wollastonite ($CaSiO_3$)	%	97.00	97.5	97.0

The chemical analyses of the concentrate obtained on different ore types are shown in Table 30.3.

A new process was tested on several ores from Finland and USA with good wollastonite grade and recovery.

30.4 Major producing countries

USA has two large wollastonite operations including Willsboro and Gouverneur.

Willsboro is one of the largest operations in the world and is located at the Fox Knoll Mine near Willsboro, New York. Operation started in 1945. The ore contains 55–65% of wollastonite. The ore contains garnet as a major impurity. The ore is crushed to 16 mesh in three stages followed by high intensity magnetic separation to remove garnet.

Gouverner operation. The ore is characterized by low levels of iron and high silica and alkali content. Vanderbilt produces three different grades of wollastonite, which is used in a number of applications in the ceramic industry and as fillers in the paint and rubber industry.

Lappeenranta, Finland is the second largest operation in the world. The deposit, which contains limestone, dolomite, and wollastonite is located in south-east Finland at Lappeenranta.

The wollastonite crystals are typically needle-like, up to 0.5 mm long and 0.2 mm wide. The wollastonite content of the ore is between 18% and 20%.

Table 30.4 Chemical Composition of the Major Producers of Natural Wollastonite

Element	New York, USA	New York, USA	Finland	Finland	USSR	Turkey	India	Jilin, China	Anhul, China
CaO	47.0	46.1	47.13	40.49	40.64	47.5	48.02	43	46.1
SiO_2	50.0	50.2	51.55	52.06	37.93	47.95	48.77	50	50.59
Fe_2O_3	1.0	0.15	0.58	0.63	1.56	0.58	0.43	0.08	0.38
MgO	0.3	1.86	0.10	0.60	1.7	0.78	0.06	0.04	1.03
Al_2O_3	1.0	0.21	0.08	0.51	3.66	2.37	0.66	0.05	0.33
LOI	N/A	0.94	0.42	6.16	13.82	0.52	1.68	2.0	1.3

At present, the plant floats first calcite and dolomite followed by wollastonite flotation using modified secondary amine.

Concentrate grade of between 84% and 95% wollastonite grade is produced.

Mexico has several operating plants in the province of Zacatecas. A total of four producing plants are in operation at present. In some plants, wollastonite is sorted, crushed, and milled to produce four different grades.

Other producers: Wollastonite production is known in a number of other countries but on a relatively small scale. These countries include Namibia, Japan, Turkey, India, and China. Chemical composition of the major producers of natural wollastonite is shown in Table 30.4.

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CHAPTER

31

Beneficiation of Zircon Containing Ores

CHAPTER OUTLINE

31.1 Introduction

Zircon minerals belong to the orthosilicate group together with topaz, kyanite, tourmaline, olivine and others. The beneficiation of zircon largely depends on the type of deposit as well as mineral composition. In most cases zircon is found in heavy minerals that contain titanium mineral sand as well as rare earth oxides.

Zircon is acid insoluble, and normally associated with small amounts of hafnium and yttrium. Zirconium in the lattice may be replaced by iron and or calcium.

There are two principal methods for flotation of zircon from heavy mineral sand. These include: (1) bulk flotation of heavy minerals followed by depression of titanium and zircon flotation, and (2) depression of zircon and flotation of other valuable minerals.

In this chapter, a summary of different beneficiation methods will be described which is useful for the treatment of heavy mineral sand containing zircon and also beneficiation of zircon from hard rock.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00031-2

31.2 Zircon minerals and deposits

The major zircon minerals include zircon $Zr(SO_4)$ and eudialyte.

Zircon has a hardness of 7.5 and specific gravity of 4.7. Color of zircon can be yellow, green, brown, and usually appears as tetragonal crystals.

The eudialyte, a zirconium silicate of a complex composition, usually contains Rare Earth Oxides (REO) minerals and niobium. On average, eudialyte contains 13.5% ZrO_2, 0.6% Nb_2O_5, and 2.5 total REO.

The mineral deposits found in Greenland and Russia have complex mineral composition. The main gangue minerals include: (1) aegirine, (2) nepheline, (3) sodalite, and (4) syenite.

Over 90% of zircon is contained in a heavy mineral sand and is associated with iron oxides. Titanium minerals (ilmenite, rutile) and rare earth minerals (monazite and other).

Some zircon is also found in placer deposits in Canada and USA.

31.3 Flotation development of zircon

31.3.1 Introduction

Extensive research work on flotation properties of zircon was conducted by a number of researchers [1,2]. It was concluded that zircon may be floated with anionic and cationic collectors over a wide range of pH values. Good zircon flotation was achieved with sodium dodecyl sulfate at pH 2.5 and with dodecylamine chloride at pH 10.0. Using C_{18}-fatty acids, the range of flotation of zircon can be extended from pH 4.0 to 9.0.

It has been shown that [3] zircon can be activated by sulfate, phosphate, and oxalate ions in the acid pH region and by ferric iron when floating with sodium oleate in the alkaline pH.

31.3.2 Flotation of microlithe and zircon from pegmatite tin deposit

There are several pegmatite-type tine deposits in South Asia that contain zircon and microlithe ($Ca_2Ta_2O_6$). Studies of zircon microlithe flotation and zircon microlithe separation were performed at the University of Aachen, FRG [4]. In these studies, collector type and zircon particle shape were examined.

Collectors examined, alkyl-sulfosuccinamate, oleic acid, and dialkyl-phosphoric acid, have proven to be the most selective collectors for zircon, while microlithe remained in the zircon tailing. The effect of sulfosuccinamate on grade and recovery of microlithe in the zircon tailing is shown in Figure 31.1. Flotation was performed at pH 4.0. The recovery of microlithe was reduced at a higher collector addition due to the fact of the portion of microlithe reported to the zircon concentrate.

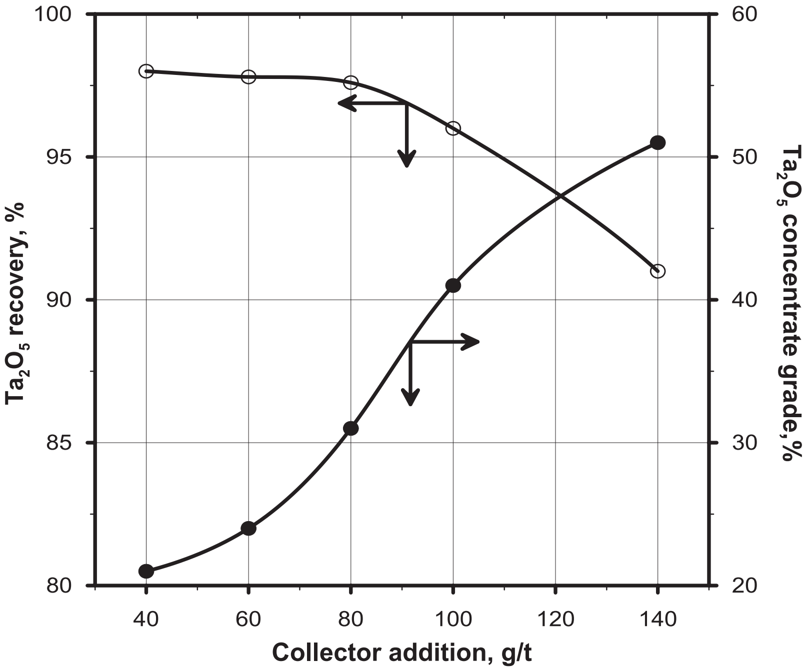

FIGURE 31.1

Effect of the level of collector on Ta_2O_5 grade and recovery in the zircon flotation tailing.

The effect of the different collector types on zircon flotation is shown in Figure 31.2. Results obtained indicated that each collector gave high zircon recovery at a relatively low addition rate of collector.

In these experiments the flotation pH was maintained at pH=4.5.

The shape of zircon particles had an effect on zircon flotability. Experimental data indicated that a prismatic shape (long and short) floated faster than elliptic and round particles. This is due to the fact that round and elliptic zircon particles have a rough surface with partial oxidation.

31.3.3 Flotation studies of zircon and tantalum niobium from hard rock ores

A large hard rock tin deposit in Pitinga, Brazil exists which also contains zircon and tantalum/niobium.

Tin is recovered using gravity, and intermediate product contains zircon, tantalum, and niobium with an average grade of 2.4% Nb_2O_5, 0.23% Ta_2O_5, and about 17% ZrO_2. Mineralogical studies have shown that zircon contains both thorium and uranium. Other gangue minerals present were quartz, feldspar, plagioclase, and amphibole. All minerals were coated with iron hydroxide.

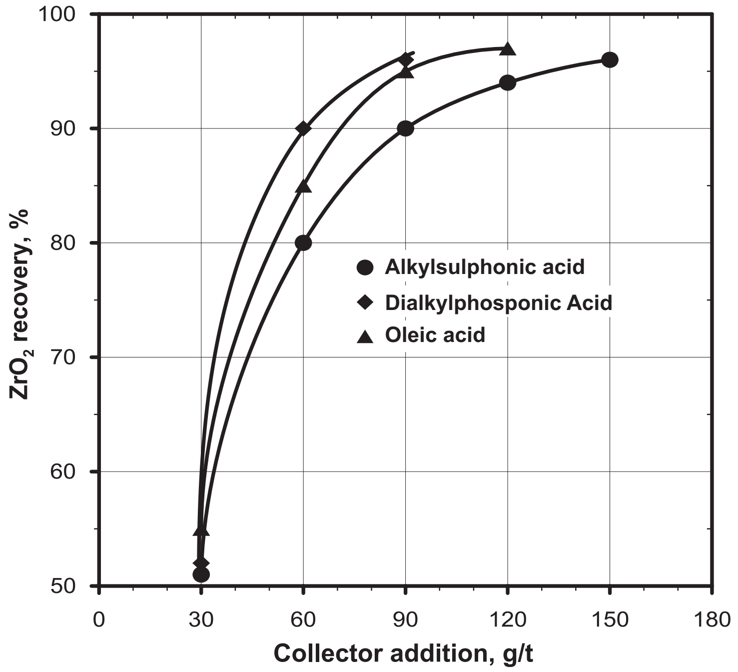

FIGURE 31.2

Effect of levels of collectors on zircon recovery from pegmatite tin tailing.

Table 31.1 Direct Zircon Flotation Results Using Modified Fatty Acid

		Assays %		% Distribution	
Product	**Wt %**	**ZrO_2**	**Nb_2O_5**	**ZrO_2**	**Nb_2O_5**
ZrO_2 rougher concentrate	58.21	22.2	3.38	76.9	84.1
ZrO_2 rougher tail	36.40	10.4	0.96	22.5	14.9
Magnetics	5.740	1.98	0.42	0.6	1.0
Feed	100.0	16.82	2.34	100.0	100.0

Experimental work was conducted to flot zircon and depress tantalum niobium. In these experiments, tantalum and niobium were depressed with starch and zircon was floted with a variety of collectors including fatty acids, secondary cocoamines, and sulfosuccinamate. In none of the experiments was selective zircon flotation achieved. Typical zircon flotation results are shown in Table 31.1.

Selective flotation of tantalum/niobium from zircon was examined in detail [5]. The variables examined include: (1) type of zircon depressant, (2) type of tantalum–niobium collector, and (3) flow sheet configuration.

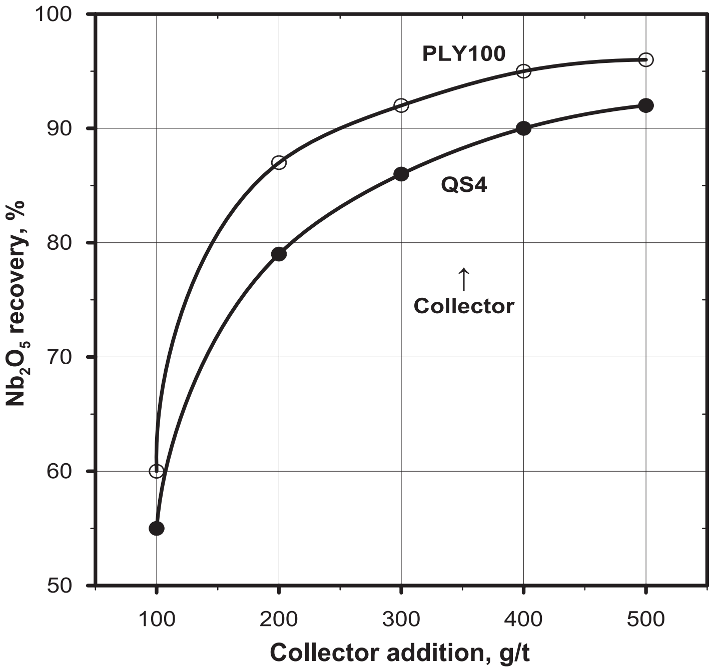

FIGURE 31.3

Effect of level of collector QS4-1 and collector PLY100A on niobium rougher recovery.

A number of new tantalum niobium collectors were examined including collectors, QS series and PLY series. The QS4 series of collectors are a mixture of secondary amine acetate and imidazoline modified with different surfactants. The PLY100 series of collectors are a mixture of phosphoric acid esters, Ethofat 242/25 and imidazoline. The effect of the levels of these collectors on niobium recovery is illustrated in Figure 31.3.

In these experiments, oxalic acid–H_2SiF_6, a zircon depressant system was used.

The oxalic acid in the presence of fluorosilicic acid was an effective zircon depressant. The effect of levels of oxalic acid on zircon depression is shown in Figure 31.4. In these experiments, levels of H_2SiF_6 were kept constant at 300 g/t.

The final flow sheet established is shown in Figure 31.5. The most important feature of this flow sheet is removal of iron hydroxide coating, which is achieved with scrubbing in the presence of acidified silicate and surfactant.

31.4 Beneficiation of heavy mineral sand containing zircon

Most of the zircon was produced from heavy mineral sand. The heavy mineral sand deposits are located in Australia, Thailand, India, Sri Lanka (Africa) and USA. The major minerals of economic value include zircon, titanium minerals, and rare earth

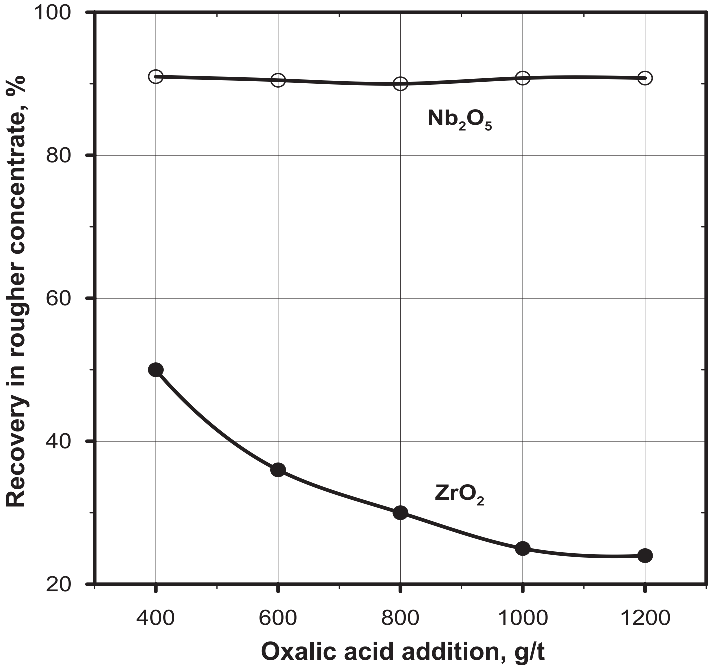

FIGURE 31.4

Effect of levels of oxalic acid on zircon depression during tantalum–niobium flotation.

oxides. Most of the research work was devoted to the separation of individual minerals including titanium, monazite, and zircon.

In beneficiation of heavy mineral sand, physical separation including gravity, magnetic separation and electrostatic separation, and flotation were practiced. Combination of physical separation and flotation is often practiced in operating plants.

31.4.1 Description of heavy minerals flotation processes for recovery of valuable minerals

There are a number of processes developed for beneficiation of zircon and other valuable minerals from heavy mineral sand. Some of the most important processes using flotation techniques are described in this section.

The zircon rutile sand from Byron Bay in Australia is beneficiated using rutile depression and the zircon flotation method [6]. This method improves conditioning gravity concentrate in the presence of a 300–500 g/t mixture of oleic and stearic acid at 95 °C for 20 min at alkaline pH followed by three water washes and an acid wash at room temperature. The flotation of zircon was then carried out at pH 1.9 using only frother; using this method about 95% zircon was recovered at about 66% ZrO_2 grade.

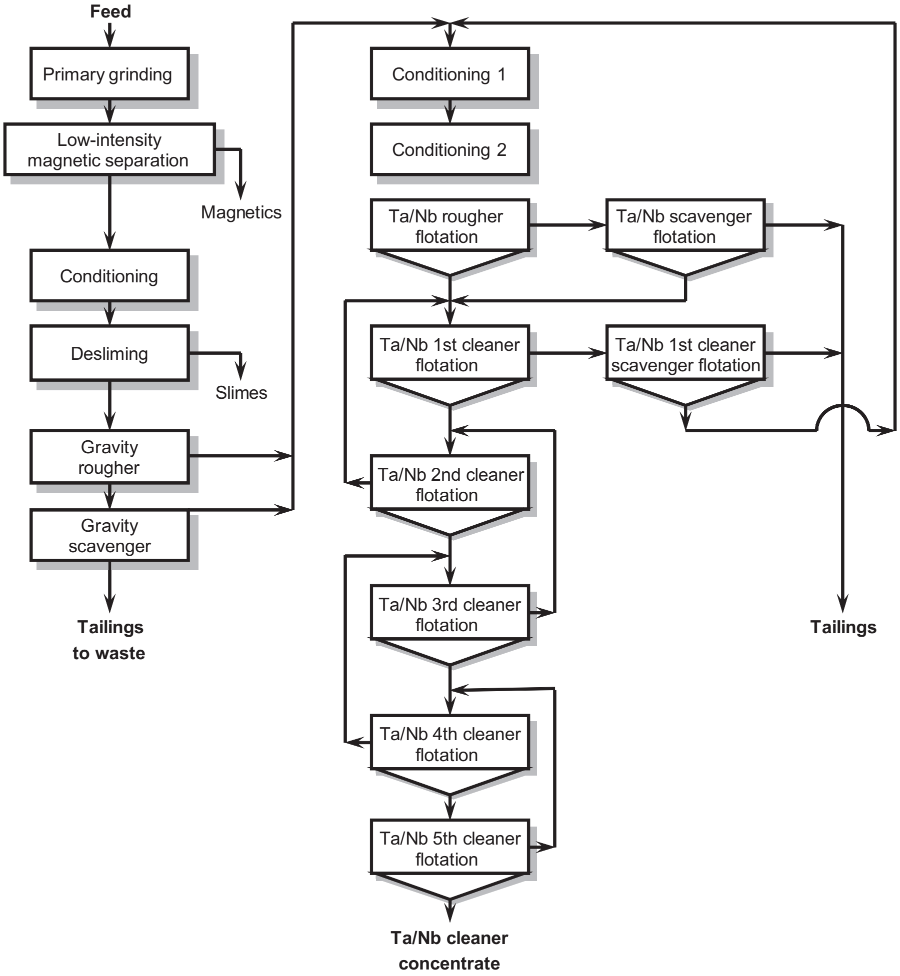

FIGURE 31.5

Final flow sheet developed for the beneficiation of tantalum/niobium zircon using zircon depression and tantalum–niobium flotation.

Wimera Heavy Mineral Sand: the Wimera deposit is located east of Melbourne, Australia [7].

The mineral sand has a complex mineral composition. The major valuable minerals are zircon, rutile, ilmenite, monazite, and yttrium. After a number of years a process has been developed for production of REO concentrate, ZrO_2 concentrate, ilmenite and rutile concentrate. This process involves several steps including:

- sand preparation;
- bulk ZrO_2, TiO_2, REO flotation;

- ZrO_2/REO titanium separation; and
- ZrO_2/REO separation.

In some stages of beneficiation process, a new technology was introduced.

Sand preparation involves removal of 1 mm waste fraction followed by scrubbing and desliming at K_{80}—5 mm. The deslimed sand is subjected to bulk flotation.

Bulk flotation: a number of different collectors were examined in the bulk flotation circuit including modified fatty acids, diamines, and fatty amine acetate. Most of these collectors gave good recovery in the bulk flotation. Examples of bulk metallurgical results are presented in Table 31.2. In these experiments modified fatty acid was used at pH 8.5.

The pulp was conditioned with 250 g/t NaS followed by collector addition and bulk flotation.

Zircon–titanium separation from the bulk concentrate was achieved using titanium depression and zircon flotation.

The bulk concentrate was stage conditioned with NaF (120 g/t) cornstarch (200 g/t) and H_2SO_4 to pH 3.0. Zircon was floated using small quantities of amine acetate collectors. The pilot plant metallurgical results are shown in Table 31.3. Most of the yttrium and REO reported to the zircon concentrate.

The titanium is upgraded from zircon tailing using a process described in Volume 2 of the book.

Table 31.2 Standard Bulk Metallurgical Results Obtained on Wimera Sand

Product	Wt %	Assays %			% Distribution		
		TiO_2	ZrO_2	Fe	TiO_2	ZrO_2	Fe
Bulk rougher concentrate	9.16	27.44	10.36	9.27	83.7	93.8	67.7
Bulk rougher scavenger concentrate	11.76	24.33	8.58	8.27	95.3	99.7	78.1
Bulk scavenger tail	88.24	0.16	0.003	0.31	4.7	0.3	21.9
Feed	100.00	3.00	1.01	1.25	100.0	100.0	100.0

Table 31.3 Zircon–Titanium Separation Results from the Bulk Concentrate

Product	Wt %	Assays %			% Distribution		
		ZrO_2	TiO_2	Fe	ZrO_2	TiO_2	Fe
ZrO_2 concentrate	1.49	56.2	0.15	0.30	95.5	0.1	0.5
ZrO_2 comb. tails	98.51	0.04	25.26	8.3	4.5	99.9	99.5
Feed	100.00	8.8	25.1	8.2	100.0	100.0	100.0

Monazite–zircon separation: the separation was performed on zircon concentrate from the zircon–titanium separation. In this testwork the zircon was depressed and monazite was floated. The process involves feed conditioning with oxidant (NaOCl) and hydrofluoric acid (HF) followed by monazite flotation using collector emulsion EmNN at pH 9.5. This emulsion consists of 75% oleic acid, 10% ArmacHT (Akzo Nobel), and 15% Aerosol AY100.

Concentrate assaying 25% REO and 6% Y_2O_3 was produced at 92% REO and 75% Y_2O_3 recoveries.

31.4.2 Separation of aluminum silicate and zircon from heavy mineral beach sand

The beach sand that contains silica, aluminum silicate, titanium (ilmenite), and zircon are found along the seashore in Florida, USA and elsewhere. A process has been developed [7] by which alumosilicate, zircon, and ilmenite were recovered separately.

Initially ilmenite was recovered using magnetic separation. The nonmagnetic fraction is stage conditioning at 60% solids with HF and alpha sulfostereic acid followed by pulp dilution to 25% solids and zircon + alumosilicate bulk concentrate was recovered while silica reported to the tailing. The concentrate was scrubbed with NaOH to remove residual collectors followed by conditioning with dextrin and amine acetate as zircon collector at pH 8.5. Zircon concentrate was produced while alumosilicate reported to the tailing. Using this method a zircon concentrate assaying 66.0% ZrO_2 at 82% recovery was achieved. High-grade alumosilicate was also produced. The separation flow sheet is presented in Figure 31.6.

31.4.3 Evaluation of metasilicate as a zircon rutile depressant during monazite flotation

Extensive research work was performed [8] in which sodium sulfide and sodium metasilicate were used in separation of monazite from zircon and rutile. Sodium oleate and hydroxanate were used as collectors. Based on the data generated, the following was concluded.

Using sodium sulfide, a nonselective depression of zircon and rutile was achieved in the presence of either sodium oleate or hydroxamate as monazite collectors. Some improvement in the zircon–rutile depression using Na_2S was achieved at pulp temperature of between 60 °C and 70 °C.

Sodium metasilicate was shown to be excellent zircon–rutile depressant while has a little effect on monalite flotation. Figure 31.7 shows the effect of the level of sodium metasilicate on flotation of zircon, rutile, and monazite.

The effect of temperature was also examined. Higher flotation temperature has no significant effect on individual mineral flotation.

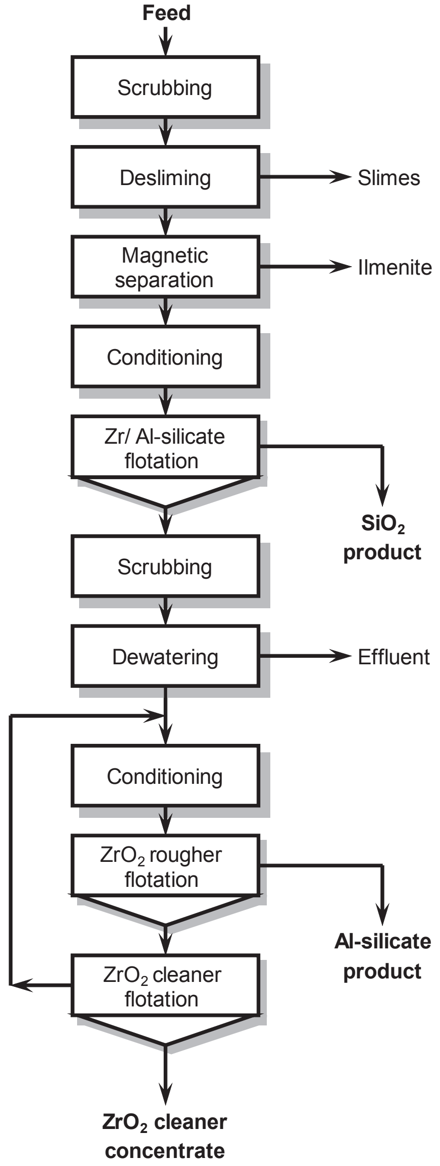

FIGURE 31.6

Flow sheet used in zircon–alumosilicate separation.

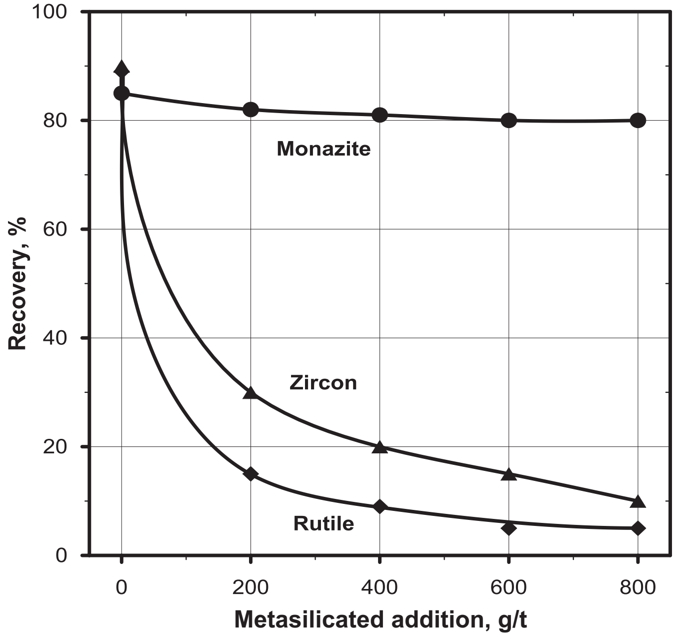

FIGURE 31.7

Effect of level of sodium metasilicate on zircon, rutile, and monazite flotation.

31.5 Beneficiation of eudialyte containing ores

Eudialite and yttrium are a valuable source of rare earth mineral. There are only several sources of eudialite deposits including a deposit in Greenland and Kola Peninsula in Russia.

Eudialite is a zircon silicate of a relatively complex composition, which includes REO, yttrium, and niobium. Usually the main gangue minerals are aegirine, nepheline, and feldspar. Pure eudialite contains between 6% and 13% ZrO. Eudialyte is also paramagnetic and can be recovered by magnetic separation.

Extensive research was performed using flotation techniques to recover eudialyte [9]. The ore used in the study assayed 1.66% (Zr, HF) O_2, 0.2% Nb_2O_5, 0.49% REO. The ore also contained significant quantities of aegirine, nepheline, and feldspar.

Using sodium oleate, aegirine, nepheline, and eudialite floated readily. However, aegirine flots selectively using fatty acid in alkaline pH (9–10.5).

Eudialite flotation performance was studied using a mixture of the alkyl phosphoric acid based on primary fatty alcohol fraction C_{10}–C_{18} (Collector SINTAF).

The effect of the SINTAF collector on flotation of different minerals as a function of pH is illustrated in Figure 31.8.

Flotation of aegirine was performed in alkaline medium at pH 9–10 using fatty acid soap as a collector. About 37% by weight was removed [11]. The aegirine concentrate contained 73% pyroxene, 6% amphibole, and 20% feldspar with nepheline.

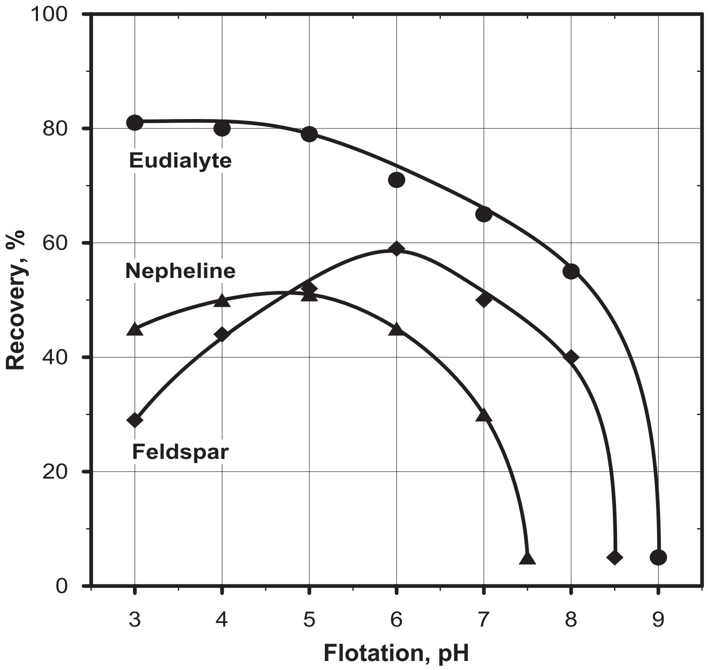

FIGURE 31.8

Flotability of eudialyte, nepheline, and feldspar with SINTAF as a function of pH.

The aegirine tailing is subjected to eudialite flotation using the flow sheet shown in Figure 31.9. The collector used was SINTAF at acid pH (3–4) controlled by sulfuric acid.

The metallurgical results obtained are summarized in Table 31.4.

Another process developed for beneficiation of Greenland eudialite ore [10] involves flotation and high-gradient magnetic separation. The principal gangue minerals in the ore were aegirine, albite, arfvedsonite, and feldspar. The beneficiation process involves grinding the ore to 100 mesh nominal size followed by desliming. From deslimed ore, albite and aegirine were floted using modified fatty acid (Neofat 92-04). The modifying agents were NaF and Na_2S. The aegirine tailing was thickened followed by high-gradient magnetic separation. The beneficiation flow sheet is presented in Figure 31.10.

Metallurgical results obtained in the pilot plant are shown in Table 31.5.

The magnetics (eudialyte product) assayed 5.6% total REO + 0.3% Nb_2O_5.

31.6 Chemical composition for zircon grades

Zircon grade is based on zirconia (ZrO_2) + hafnia (HfO_2). There are three main commercial grades of zircon. The chemical compositions of these commercial grades are shown in Table 31.6.

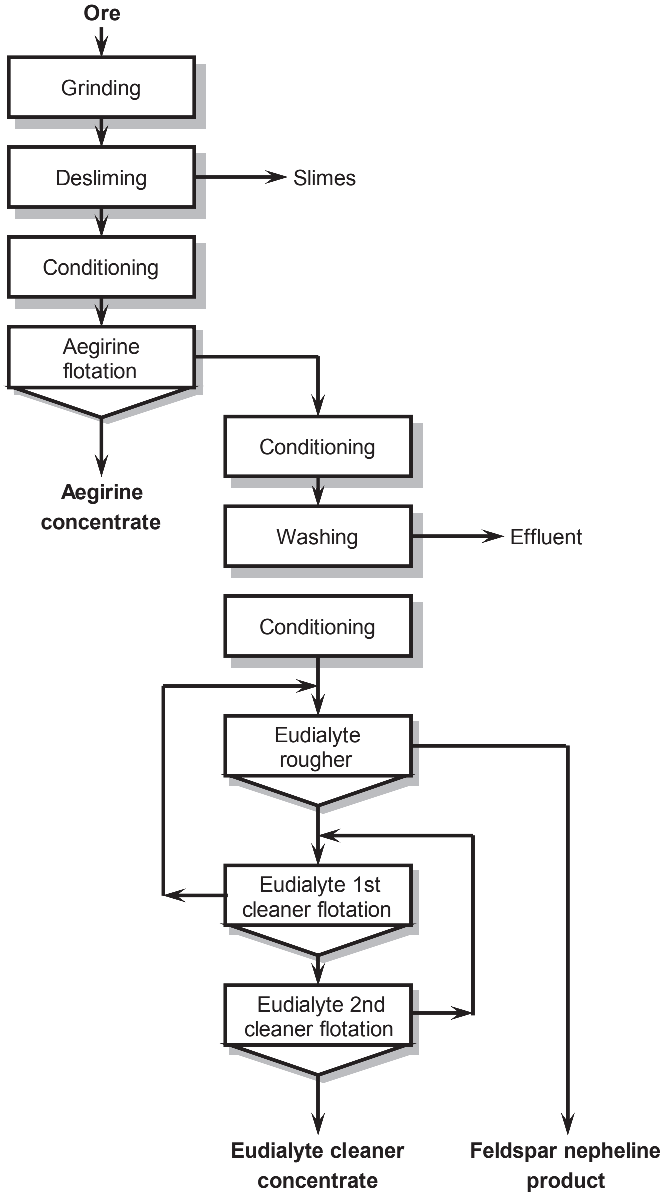

FIGURE 31.9

The flow sheet developed for eudialite flotation.

Table 31.4 Eudialyte Metallurgical Results

Product	Wt %	Assays % ZrO	% Distribution ZrO
Eudialite concentrate	11.5	10.18	71.7
Aegirine concentrate	37.6	0.71	16.4
Eudialite tailing	43.2	0.18	4.8
Slimes	7.7	1.52	7.1
Feed	100.0	1.63	100.0

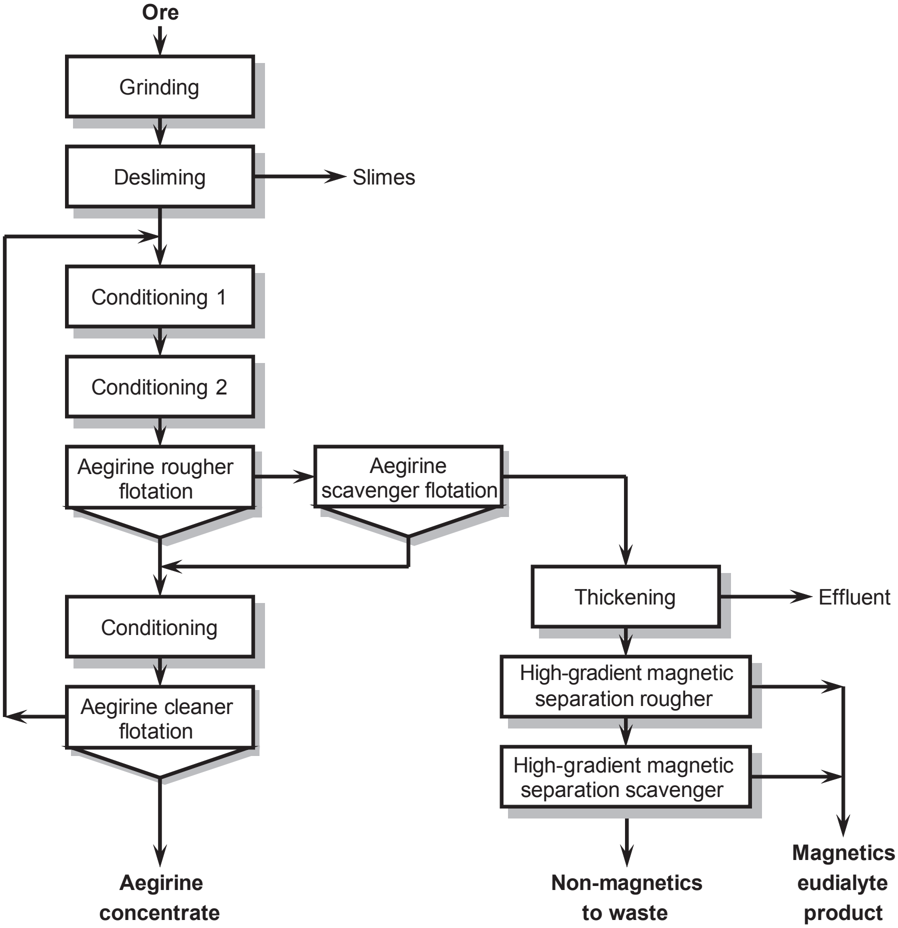

FIGURE 31.10

Flow sheet used for beneficiation of eudialyte from Greenland.

Table 31.5 Metallurgical Results Obtained in the Pilot Plant

Product	Wt %	Assays %		% Distribution	
		ZrO_2	Y_2O_3	ZrO_2	Y_2O_3
2 Tesla magnetics	16.00	4.75	0.48	70.7	73.4
2 Tesla nonmagnetics	51.5	0.37	0.038	17.7	17.1
Albite, aegirine concentrate	28.9	0.28	0.026	7.7	5.3
Slimes	3.6	1.18	0.13	3.9	4.2
Feed	100.0	1.08	0.11	100.0	100.0

Table 31.6 Chemical Composition of Commercial Grades of Zircon

Element	Premium Grade (%)	Intermediate Grade (%)	Standard Grade (%)
ZrO_2+HfO_2 min	66.0	65.5	65
TiO_2 max	0.1	0.03	0.25
Fe_2O_3 max	0.05	0.10	0.12

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CHAPTER

Beneficiation of Feldspar Ore

32

CHAPTER OUTLINE

32.1 Introduction

The feldspar may be divided into two of the following main groups: (1) orthoclase or microcline or (2) plagioclase, an isomorphous mixture of albite and anorthite.

Albite and microcline are the most important commercial feldspar but the products usually contain varying proportions of the other members of the system. The feldspar containing ores are relatively complex and equally contain mica, spodumene, quartz, and other ferro silicate. The ore reserves of feldspar worldwide are large but supplies of pure feldspar are not sufficient. In most of the cases, beneficiation of feldspar ores involves flotation. In this chapter, the beneficiation of feldspar using the flotation technique is presented.

32.2 Ore and minerals of feldspars

There are varieties of ores that contain feldspar minerals. These include, pegmatites, ores of valianogemic origin and also some of heavy mineral sand. Feldspar containing ores contain, in addition, mica, lithium minerals, silica, and sometimes iron silicates. The most important feldspar minerals are:

- Albite: $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$
- Microcline: $K_2O \cdot Al_2O_3 \cdot 6SiO_2$

Albite is a major source of soda feldspar while microcline is a source of K–feldspar. There is also an important lower temperature form of potassium feldspar. Feldspar can also be divided into a number of compositional series including anorthite, sanidine, andesine, and labradorite.

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Feldspars are found in a wide variety of geological conditions and are more widespread than any other mineral group. They occur in granites pegmatites together with quartz and mica minerals.

It should be noted that feldspar is a general term applied to a group of minerals that are silicates of aluminum, combined with potassium, sodium, or calcium or a mixture of these elements.

32.3 Flotation properties of feldspar minerals

Flotation of feldspar has been the subject of numerous studies over the past several decades. Most of the fundamental work on feldspar flotation has been concerned with the mechanism of fluoride activation at low pH. The explanation regarding fluoride activation over a number of years included the following:

- Cleaning mineral surfaces by dissolving amorphous layers [1].
- Formation of SiF_6^{-2}: amine complex in solution, which absorbs on aluminum atom surface [2].
- Formation of a potassium or sodium silicofluoride layer at the mineral surface. This layer might be expected to be negatively charged in the presence of an excess of potential—determining silica fluoride ions in solution [3].

In the case of complex ores of granites and pegmatites, the ore contains mica, spodumene, and other iron-containing minerals. From these ores, first mica is recovered followed by lithium flotation. From the lithium tailing the feldspar silica separation is carried out using HF as an activator and amine collector.

In this case, mica is removed first. There are two possible methods of mica prefloat:

One method is to float mica under acid conditions with a small amount of amine collector. Good mica removal is achieved at pH 2–3, using 280 g/t coco amine (with chain length C12) and with additions of kerosene and frother MIBC. Another reagent used is trimethylamine at pH 4.6 controlled with sulfuric acid.

The second method for mica removal involves a cationic/anionic float at pH 9.0–10.0 using sodium carbonate and lignin sulfonate to depress quartz and feldspar. Collector used was a mixture of oleic acid and tallow amine.

After mica removal, the flotation of feldspar is performed in an acid circuit. Usually after mica is removed the feldspar is then floated from the quartz. Feldspar, in fact, is more floatable than quartz under acid conditions (i.e., pH 2.0–3.5) with the additions of HF. This method is a major method in production of feldspar.

A typical method [4] for feldspar flotation after mica prefloat involves desliming of mica tailing than conditioning for 10 min with 1.7 kg/t HF and 2.0 kg/t tallow (C18) amine acetate plus fuel oil followed by feldspar flotation. Magnetic separation of feldspar concentrate was performed to remove residual iron.

The amount of HF requirements depends on the type of ore treated. If the feldspar is pure and unaltered it will require small quantities of HF, but weathered feldspar would require a larger quantity of HF.

32.4 Feldspar quartz separation without use of HF acid

A number of studies were conducted in which feldspar was floated without use of HF [5,6]. The process described the uses of a mixture of cationic and anionic collectors in an acid circuit of about pH 2 without use of HF. Alkyltrimethylene diamine acetate together with sodium petroleum sulfonate are used as a collector, and acid pH is concentrated with either sulfuric or hydrochloric acid. Another collector suitable for feldspar flotation without the use of HF is Duomin TD6 (*N*-tallow 1, 3 propylene diamine dioleate) with carboxylate anionic group instead of sulfonate gave good separation results.

The molar ratio of amine/cationic collector has a significant effect on feldspar flotation. Figure 32.1 shows the effect of molar ratio on plagioclase and orthoclase flotation recovery.

In these experiments ArmacT (tallow fatty acid primary acetate), as a cationic collector and sodium petroleum sulfonate (Reagent 308) were used.

An optimum ratio (anionic/cationic) of 0.5:1.0 in the case of plagioclase and extending to 1.5 for orthoclase can be seen from the figure.

Another method of feldspar flotation involves the use of activators Ca(II) and Al(II) in the presence of sulfonate collectors. In the experimental work alkylbenzene sodium sulfonate was used. The effect of activators as a function of pH on flotation of albite is presented in Figure 32.2. From the figure it can be seen that calcite activation is more pronounced than alumina. Higher cation concentration improves recovery of albite.

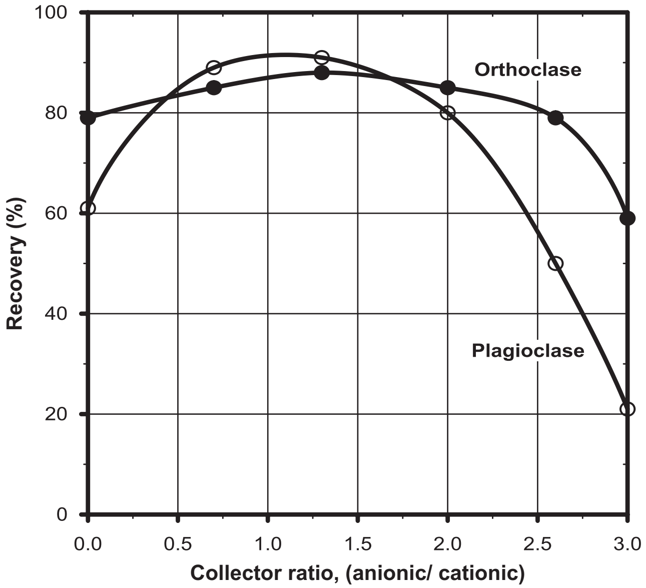

FIGURE 32.1

Effect of collectors ratio on feldspar flotation.

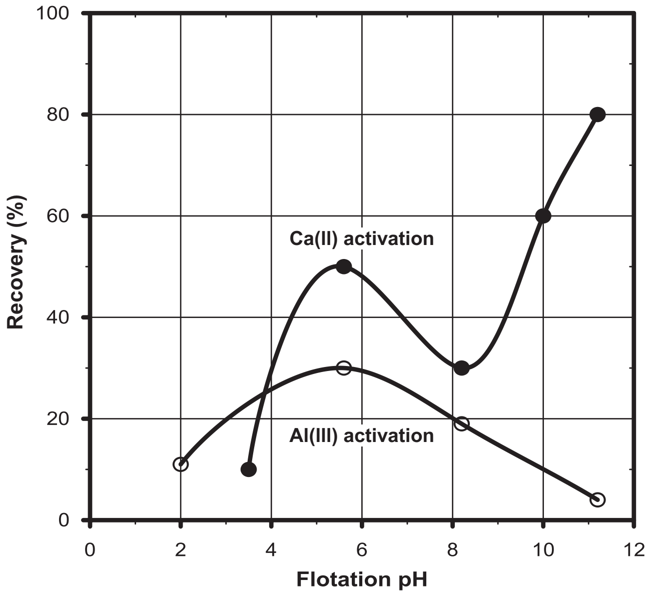

FIGURE 32.2

Activation of albite as a function of pH.

It was concluded that flotation of the minerals of the plagioclase group without use of HF increases in the order of albite + labradorite + anorthite for the same collector concentration and pH.

The flotability of these minerals also increases with increasing solubility of the minerals. That is the case of flotation response intimately related to the cation release from the solid phase especially Al(III) and Ca(II).

Feldspar activation with a poly-condensation product of dicyandiamide and formaldehyde at acid pH and the subsequent flotation with an anionic collector were examined [7].

This product is manufactured by SKW, Germany under the trade name Melflock. It has been concluded that this low molecular cationic polyelectrolite has a hydrophobizing activity because of missing C–C bonds collector used in these studies of alkyl aryl sulfonate.

The effect of Melflock on separation of feldspar and quartz using sulfonate collector is illustrated in Figure 32.3.

In a study [8] conducted on the separation of feldspar kyanite from quartz, a new collector was examined. The new collector consists of a mixture of *N*-alkylenetrimethylene-diamine and anionic collector sodium petroleum sulfate. This collector was tested on several sand samples using the collector mixture in different ratios. The best results were achieved using the collector mixture in a ratio of 1:6. The effect of the level of collector mixture on kyanite and feldspar flotation is shown in Figure 32.4.

These experiments were conducted at natural pH.

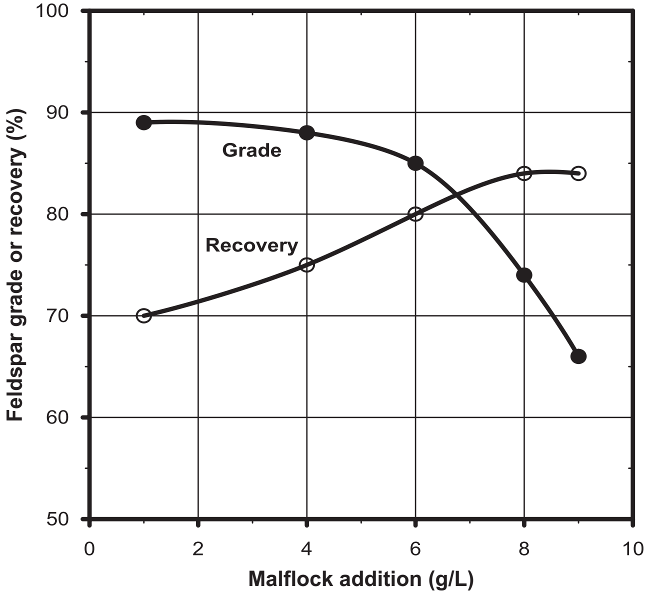

FIGURE 32.3

Effect of Melflock on feldspar grade and recovery using alkyl aryl sulfonate collector at pH 2.1 (H_2SO_4).

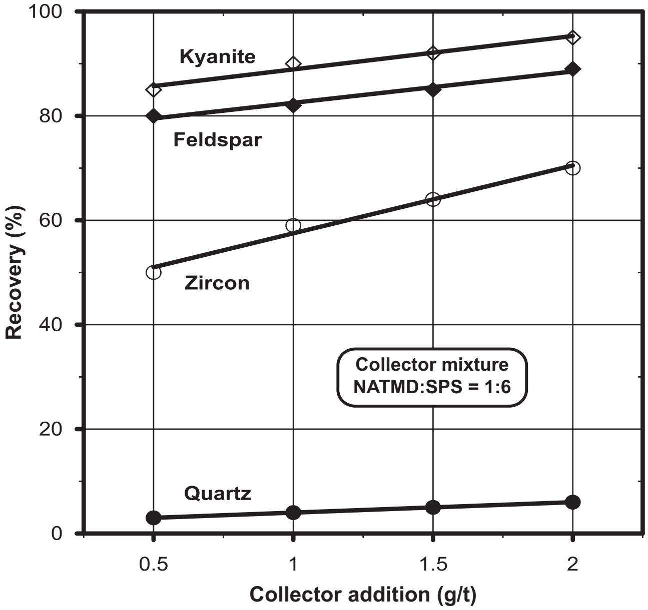

FIGURE 32.4

Effect of levels of collector mixture on kyanite and feldspar flotation from quartz. NATMD, N-alkylthremethyeone diamine; SPS, sodium petroleum sulfate.

32.5 Beneficiation practices of ores containing feldspar spodumene quartz and mica

There are a number of operating plants around the world that produce feldspar, most of which uses hydrofluoric acid and amine collector. From the complex pegmatite ore containing mica iron silicate, silica, and feldspar, sequential flotation is used. A typical example of the flotation process is Spruce Pine Ridge operation.

The ore contains mica, iron silicate, feldspar, and silica. The plant flow sheet is shown in Figure 32.5.

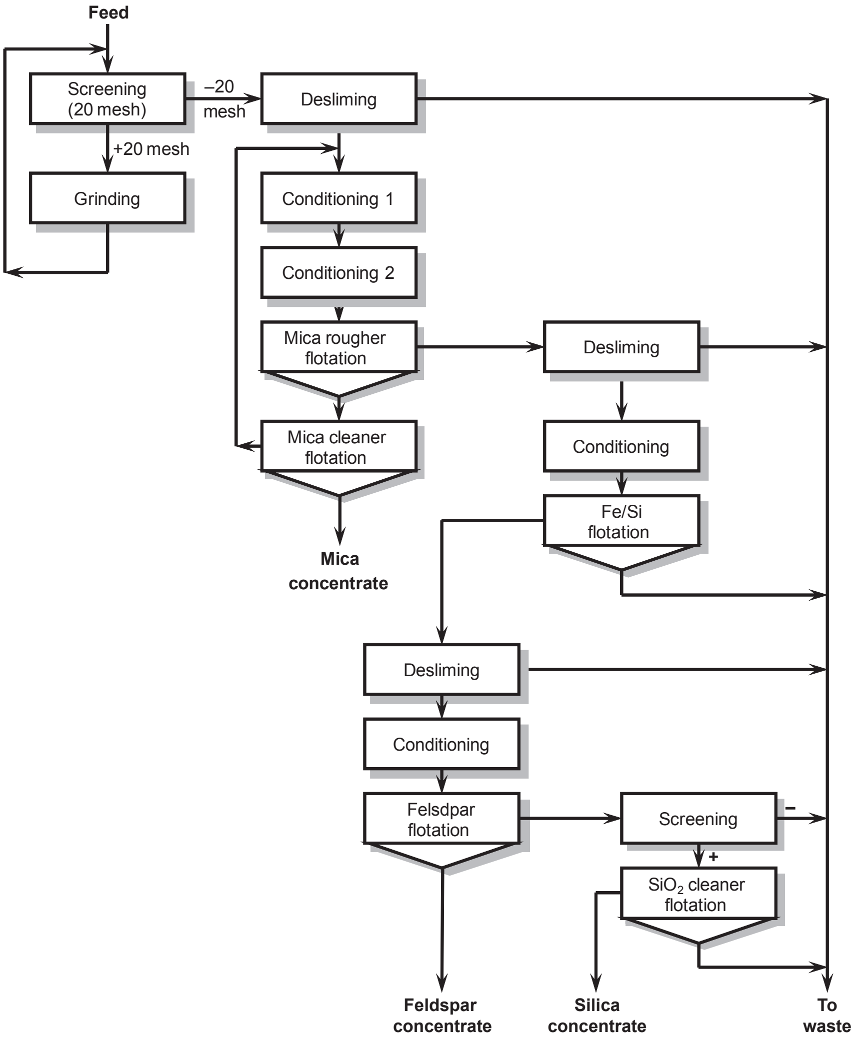

FIGURE 32.5

Flow sheet used in beneficiation of pine ridge pegmatite ore.

The flow sheet consists of four separate flotation stages. Initially mica is removed, followed by iron silicate flotation.

From the iron/silicate tailing feldspar is recovered followed by silica purification. The reagent scheme for each circuit is presented in Table 32.1.

The flotation of muscovite mica was performed using a cationic collector (Tallow amine acetate-ArmacT) at pH 3.2–3.3. The mica tail is dewatered followed by flotation of garnet, iron silicate, and residual mica using an anionic collector consisting of petroleum sulfonate (R825).

Separation of feldspar from quartz is achieved using a cationic collector (tallow amine acetate) after activation with HF.

King Mountain Operation (Carolina, US) treats spodumene pegmatite ore containing spodumene, mica, iron, feldspar, and quartz. The chemical analyses and mineral content of the ore treated are presented in Table 32.2.

The beneficiation flow sheet is presented in Figure 32.6.

Table 32.1 Reagent Scheme for Spruce Pine Ridge

Reagent	Additions g/t		
	Mica Flotation	**Fe Silicate**[a]	**Feldspar Flotation**
Modifiers and Depressants			
Sulfuric acid (H_2SO_4)	1000	200	–
Hydrofluoric acid (HF)	–	–	700
Collector and Frothers			
Tallow amine acetate	95	–	190
Petroleum sulfonate (R825)	–	250	–
Kerosene	–	–	50
Frother	20	10	15
Flotation pH	3.0–3.3	2.8–3.8	

[a] *Garnet.*

Table 32.2 King Mountain Spodumene Pegmatite Ore Analyses

Element	Assays %	Mineral Content %Wt
Li_2O	1.4–1.5	Spodumene = 15–25
Na_2O	1.2–3.8	Potash feldspar = 12–15
K_2O	2.2–2.7	Soda feldspar = 28.32
CaO	0.26–0.46	Quartz = 25–35
Al_2O_3	12.2–17.9	Muscovite and other iron minerals = 5–15
SiO_2	73.2–74	
Fe_2O_3	0.50–0.95	

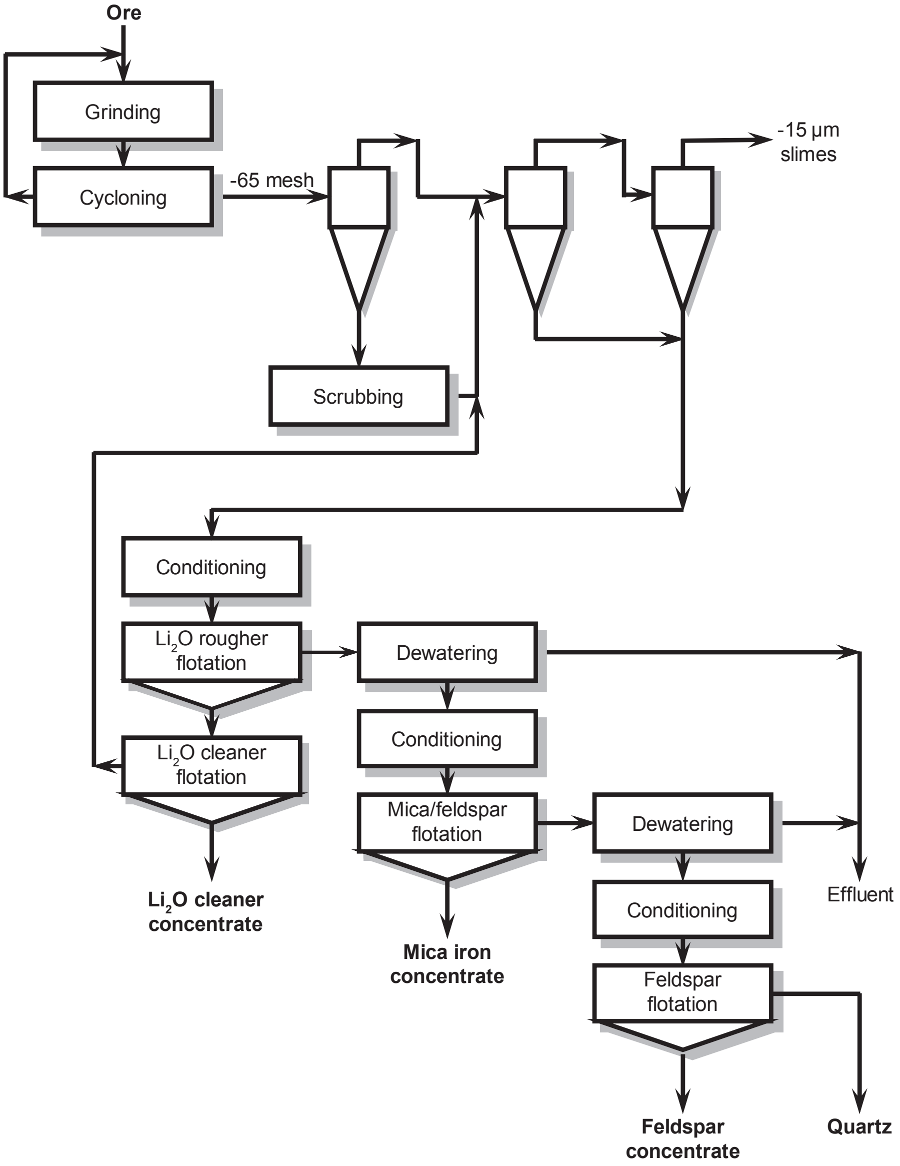

FIGURE 32.6

Flow sheet used for treatment of King Mountain pegmatite ore.

The ore is ground in the presence of NaOH. The ground ore is deslimed three times. Cyclone underflow from the first desliming stage is scrubbed. The spodumene flotation feed contained 55% solids and is conditioned with 700 g/t of tall oil fatty acid with 5–7% resin acid content at a natural pH followed by spodumene rougher flotation and a cleaning stage.

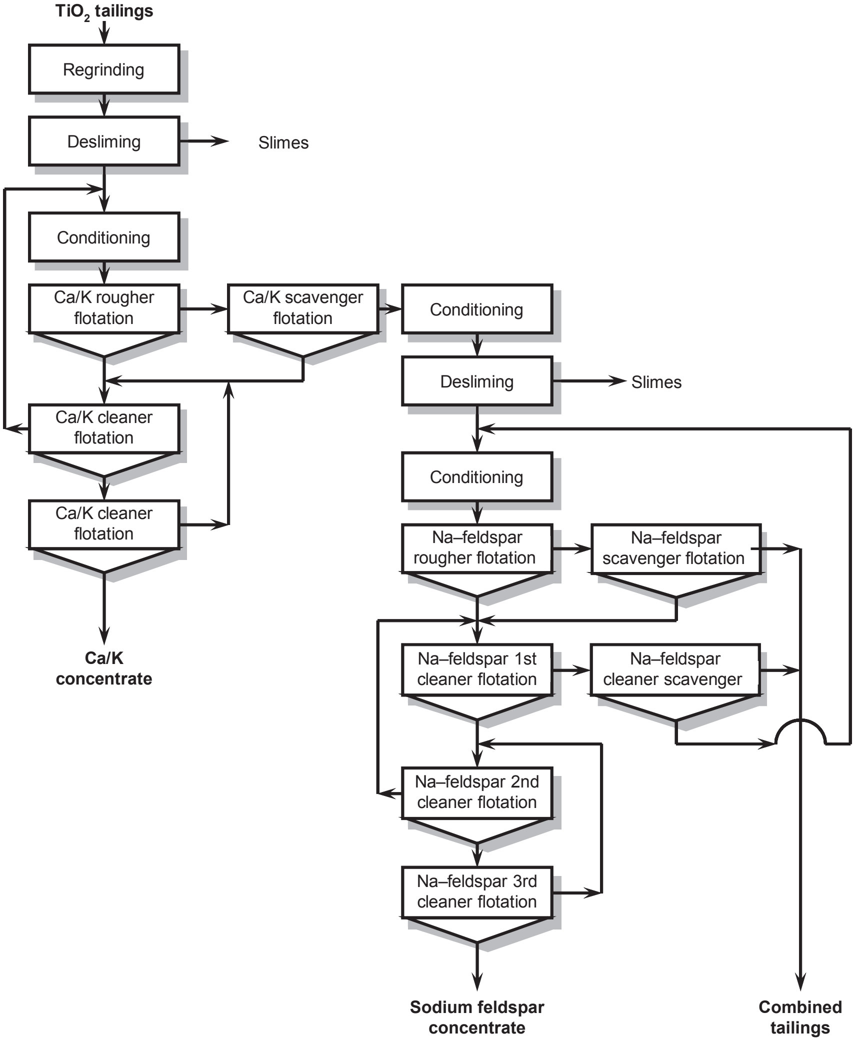

FIGURE 32.7

Feldspar flotation from complex rutile-containing ore.

A spodumene concentrate assaying 6.5% Li_2O at 88% recovery was produced.

Spodumene tailing is dewatered and reconditioned for iron mineral and mica removal. Flotation was performed using petroleum sulfonate in an acid circuit.

Feldspar flotation was performed using a nonfluoride reagent scheme [9].

The white mountain titanium deposit in Chile contains significant quantities of feldspar in addition to rutile. Research work was performed on rutile flotation tailing [10]. The titanium tailing had a relatively complex mineral composition. The main constituents of the tailing were albite (46.7%), muscovite (17.0%), quartz 19%, (sericite 10%), and kaolinite (6%) (Figure 32.7). The principal carrier of iron was muscovite. There is a strong relation between K_2O recovery and iron recovery in the albite concentrate. Figure 32.8 shows these relationships.

Muscovite flotation using a standard anionic collector alone was not satisfactory. Good removal of muscovite was achieved using a collector mixture consisting of 50% tallow alkyl amine, 25% petroleum sulfonate (R825), and 25% phosphoric acid ester (SM15).

This collector was used over 85% of iron containing muscovite.

Soda feldspar flotation was performed with NaF dissolved in HCl and the collector tallow diaminopropane dioleate (Duomeen TDO). Metallurgical results from continuous tests using the described reagent scheme are shown in Table 32.3.

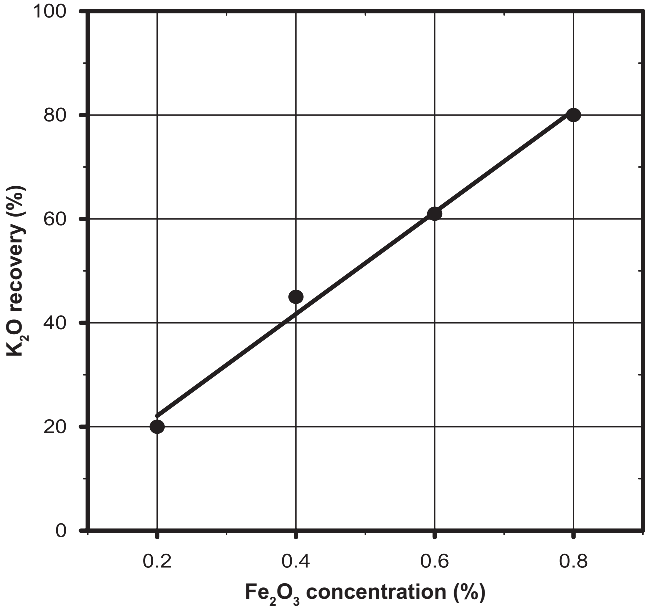

FIGURE 32.8

Relationship between K_2O and Fe_2O_3 recovery in the soda feldspar concentrate.

Table 32.3 Metallurgical Results Obtained in a Continuous Locked Cycle Test

Product	Wt%	Assays %					% Distribution		
		Na_2O	K_2O	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	SiO_2	Al_2O_3
Feldspar concentration	49.36	9.01	1.33	65.9	21.2	0.25	68.2	47.6	53.6
Combined gangue cont tailing	50.68	3.07	3.19	70.8	17.9	1.14	31.8	69.1	46.4
Feed	100.00	6.49	2.34	68.4	19.5	0.76	100.0	100.0	100.0

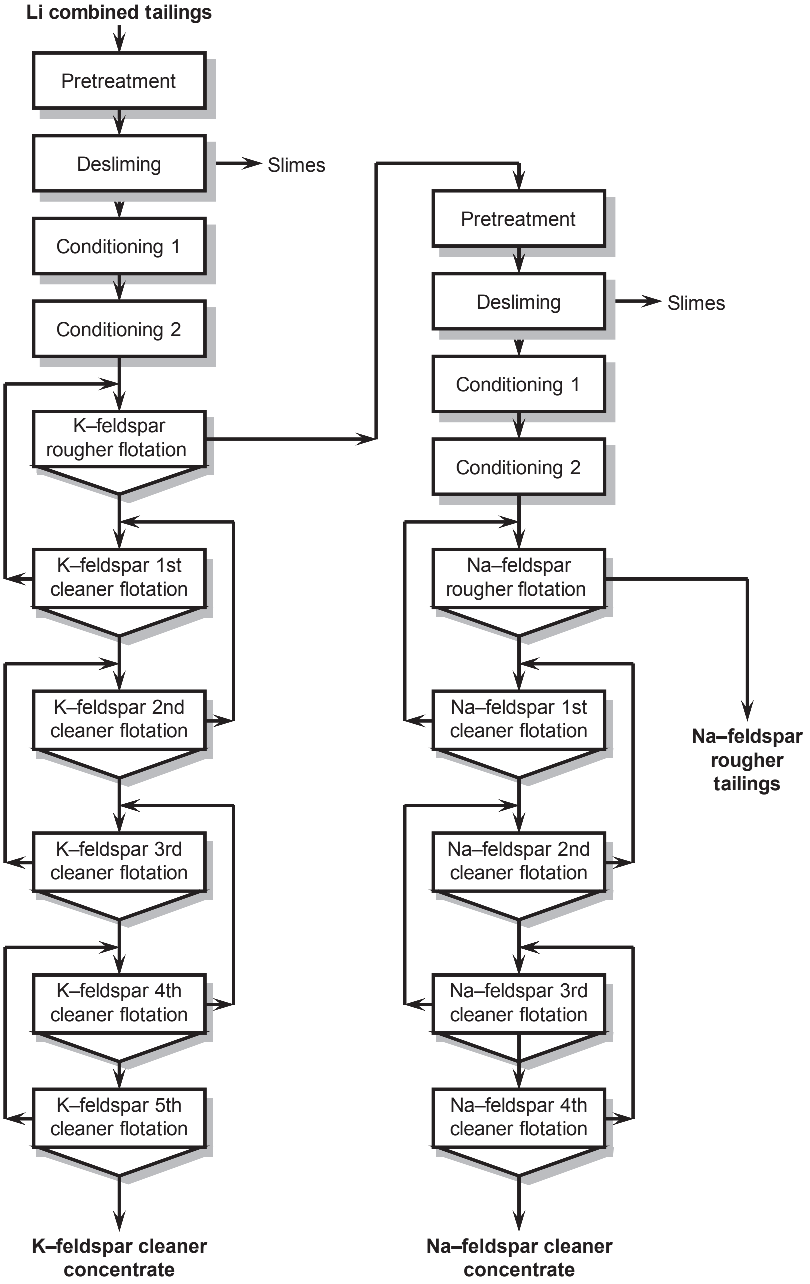

FIGURE 32.9

Feldspar sequential flotation flow sheet.

32.6 Sequential flotation of Na–feldspar and K–feldspar

Very little work was done on sequential flotation of albite (Na–feldspar and microcline K–feldspar). Some separation works have been performed by a Russian researcher [11] using monovalent salt. In these studies only partial separation was achieved.

In a research study conducted over several years, a new process has been developed by which selective separation of albite and microcline was achieved using a flotation technique [12].

It is known that monovalent salts, NaCl and KCl act as albite and microcline depressants. With these salts depression of albite is more pronounced than microcline. Using these salts it was possible to sequentially float microcline and albite. The sequential flotation flow sheet is shown in Figure 32.9.

Table 32.4 Sequential K–Feldspar and Na–Feldspar Flotation Reagent Scheme

	Reagent Additions g/t			
	K–Feldspar		**Na–Feldspar**	
Reagent	**Rougher**	**Cleaners**	**Rougher**	**Cleaners**
Depressants and Depressant				
Hydrofluoric acid (HF)	500	100	200	100
Sodium chloride (NaCl)	2000	1000	–	
Sulfuric acid (H_2SO_4)	To pH	To pH	To pH	
Reagent FR50[a]	500	–		
NaOlt[b]	500	–		
Collector				
Amine OT36 (Akzo Nobel)	500	–	50	

[a] *Dicianid Amine Formaldehyde (Na_2O Depressant).*

[b] *Pretreatment additions. Commercial name for Dodecil amine formaldehyde*

Table 32.5 Feldspar Metallurgical Results Obtained in Locked Cycle Tests

		Assays %					**% Distribution**			
Product	**Wt%**	**K_2O**	**Na_2O**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**K_2O**	**Na_2O**	**SiO_2**	**Al_2O_3**
K_2O concentration	12.25	11.7	3.40	66.2	19.1	0.04	56.6	7.5	10.3	18.5
Ne_2O concentration	50.88	2.11	10.1	67.9	19.3	0.09	42.3	91.7	44.0	77.6
Na_2O combined Tails + slime	36.87	0.075	0.12	97.3	1.31	0.12	1.1	0.8	45.7	3.8
Feed	100.00	2.53	5.58	78.5	12.6	0.10	100.0	100.0	100.0	100.0

Results obtained showed that NaCl is more selective than KCl. The NaCl is used in the final continuous tests shown in Table 32.5. The final reagent scheme developed for sequential flotation is shown in Table 32.4.

Flotation of both K–feldspar and Na–feldspar is performed at pH 3.2.

The pretreatment before desliming was done in the presence of NaOH.

Metallurgical results obtained in continuous tests using the above reagent schemes are summarized in Table 32.5.

Good separation results were achieved using sequential flotation method.

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CHAPTER

Beneficiation of Silica Sand

33

CHAPTER OUTLINE

33.1 Introduction

Silica is an important product in industrial minerals. Silica has many industrial applications in abrasives and polishes; in glass manufacturing, fillers and extenders, silica brick manufacturing as a catalyst; in specialty coatings, cleaners ceramics, electronics optics, and refractories; in ferro-silicon manufacturing and rubber.

Processing of silica of specific quality yields several types of specialty silicates. These include: (1) colloidal, (2) fumed, (3) fused, (4) high-purity ground silica, (5) silica gel, and (6) precipitated silica.

Colloidal silica is mainly used as a high-temperature binder for silicon wafer, polishing, and precipitated silica.

Fused silica is produced by fusion of very high-quality silica sand feedstock in electric arc and resistance furnaces. This converted silica can be used as a filler or electronic encapsulant.

High-purity ground silica is a product from silica sand or soft friable rocks as an amorphous silica. It is mainly used in specialty, coating, plastics, rubber, electronics abrasives, and optics.

Beneficiation of silica-containing ores depends on the type of ore. Silica sand for example, low in iron, is much in demand, for glass, ceramics, and pottery use.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00033-6

33.2 Silica sand deposits

There are a number of different silica deposits that are used in the production of a high-silica product (i.e., over 99% SiO_2). Some of these deposits are described as follows:

- Quartz veins: these deposits are extremely high-grade containing white silica crystals. These deposits occur in eastern Canada and in some places in the USA.
- Quartzite is a metamorphosed sandstone made up chiefly of quartz sand united by a siliceous cement forming low-porosity rock. Quartzite varies from white to gray and sometimes brown, red, or yellow due to the presence of small amounts of impurities.
- Some of quartzite deposits may contain up to 99% SiO_2.
- Sandstone deposits: these deposits contain significant amounts of impurities, i.e., Fe_2O_3, Al_2O_3, and CaO. Origin of these deposits is a paleozoic sediment. Also these deposits may contain clay, in a range of 5–10%.

33.3 Beneficiation of silica sand

33.3.1 Introduction

A large portion of silica is produced from quartz veins and quartz sands, while other sources include sandstone deposits. In beneficiation of silica sand, relatively simple processes are used. Some of the processes include:

- Attrition scrubbing washing
- Magnetic separation
- Heavy media separation
- Reverse gangue flotation
- Acid leaching

A combination of the above methods may be used to beneficiate sand with complete impurities.

For many applications, clean sand to over 99% silica with low impurities is required.

33.3.2 Process used in beneficiation of silica sand

33.3.2.1 Attrition scrubbing washing method

This method is usually used for beneficiation of high-grade calcite with low impurities of iron and other silicates. The flow sheet used is shown in Figure 33.1.

During attrition scrubbing caustic soda or acid was normally used depending on the type of surface coating of quartz sand.

33.3.2.2 Production of high-grade silicate using leaching process

This process was adopted by the British Industrial Sand Company for removal of iron and other impurities from sandstone deposit. In this process a little acid was used due to the fact that iron content of the sand was about 0.5% Fe_2O_3. Leaching was

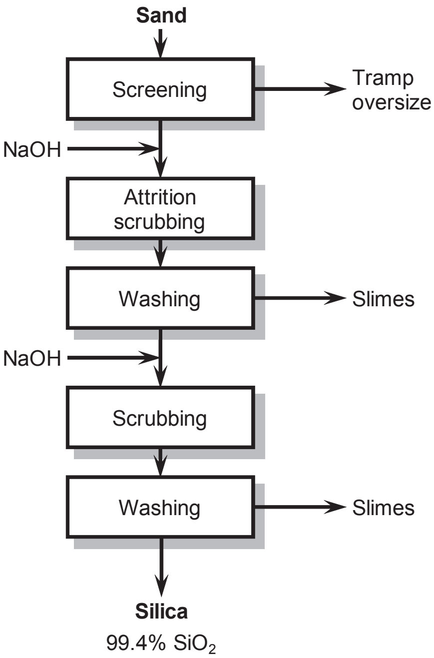

FIGURE 33.1

Attrition scrubbing washing flow sheet.

conducted in the presence of metal chloride at elevated temperature of about 50 °C. After completion of leaching, the acid and metal chloride were removed by multiple-stage countercurrent washing and acid regeneration.

The leached silica contained less than 0.03% Fe_2O_3.

The leaching flow sheet is shown in Figure 33.2.

33.3.2.3 Attrition scrubbing flotation

This method is normally used for beneficiation of silica sand that contains mica and high-iron oxides. Attrition scrubbing is usually done using acid. The beneficiation flow sheet is presented in Figure 33.3.

The flotation is performed at acid pH 2.5–3.5 and controlled with either sulfuric or hydrochloric acid. The collectors usually used are sulfonate-based collectors from Cytec 800 Series (i.e., R801, R827). Using this method, iron content of the [1] silica product is reduced to about 0.06% Fe_2O_3.

Virtually all mica and alumina report to the flotation concentrate.

33.3.2.4 Beneficiation of silica sand that contains various impurities—three stage flotation method

Some of the silica sand deposits from the USA and Canada contain impurities such as pyrite, iron oxides, and feldspar. Beneficiation of silica from these deposits involves

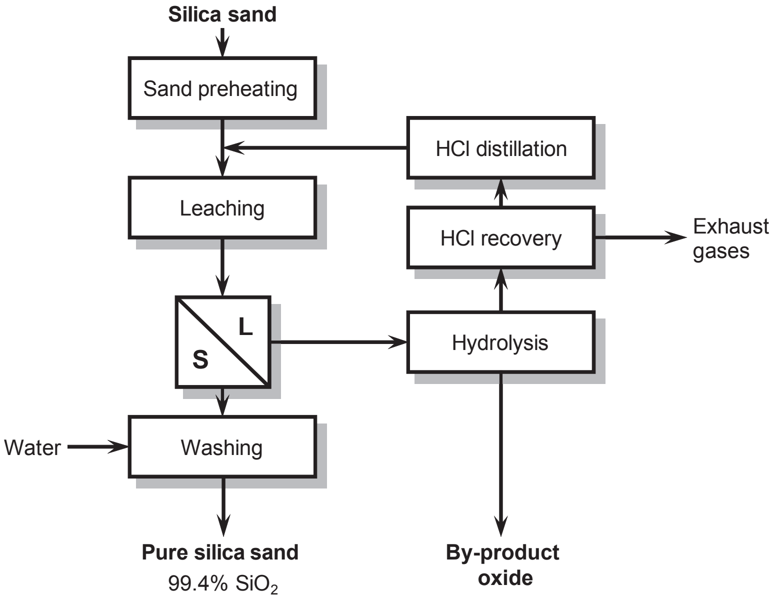

FIGURE 33.2

Flow sheet used in leaching of silica sand.

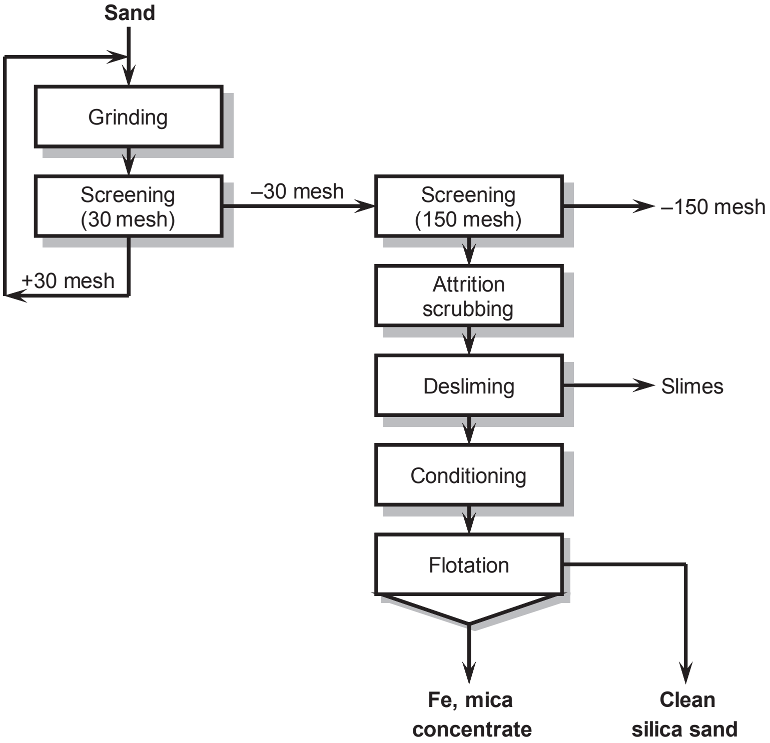

FIGURE 33.3

Flow sheet used in beneficiation of silica sand using attrition scrubbing flotation.

attrition scrubbing followed by three-stage flotation process [2]. In this research study a number of different reagent schemes have been examined, in various stages.

A generalized flow sheet for beneficiation of silica sand with various impurities is shown in Figure 33.4.

The sulfide flotation was accomplished using either xanthate or mercapto type of collectors at slightly acidic pH (i.e., 6.0).

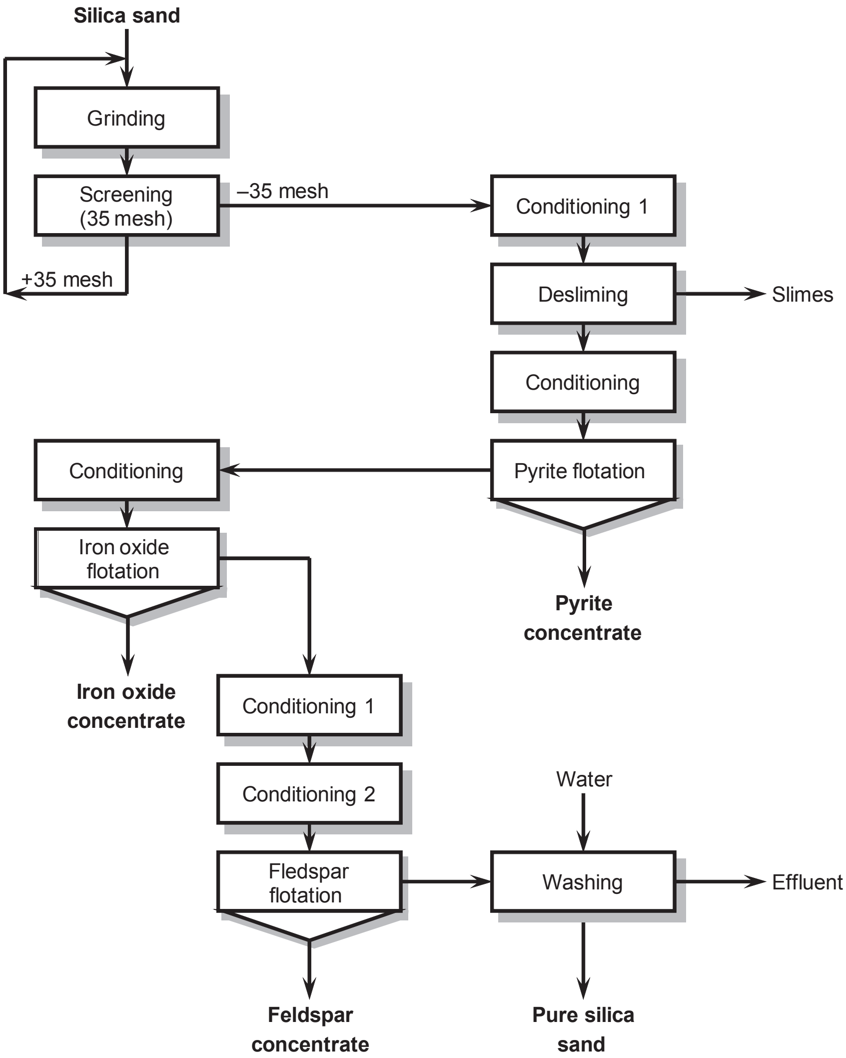

FIGURE 33.4

Flow sheet used for beneficiation of silica sand that contains pyrite, iron oxide, and feldspar.

Iron oxides are floated using natural petroleum sulfonate collectors (Aeroflot R840) [3] at pH 2.3–3.5. A high pulp density conditioning at 50% solids with reagents was used. Because hydrofluoric acid (HF) was always used as a feldspar activator, and being a hazardous chemical, an attempt was made to examine a non-HF flotation method [4]. Collectors ArmacT (Tallow amine acetate, Armac C (coco amine acetate)) and Duomeen TDO (*n*-tallow-1, 3-diaminopropene dioleate) were examined. The best metallurgical results were achieved with Duomeen TDO at pH 2.1–2.8. At this pH, it was possible to float feldspar without floating quartz.

33.3.2.5 Beneficiation of silica–kaolin sand

The silica sand used in the study consists of poorly sorted angular grains of clear quartz loosely cemented together by kaolinite clay. Lances of high-grade kaolinite were also present in the ore body.

Basically, this ore was beneficiated using attrition scrubbing and screening.

The flow sheet used is shown in Figure 33.5. The sand was first attrition scrubbed at about 50% solids for 20 min, followed by sizing. The fine fraction was deflocculated using $Na_4P_2O_7$ followed by sedimentation, where coarse clay and fine clay (i.e., 12 µm) were separated and the fine clay was bleached and dried.

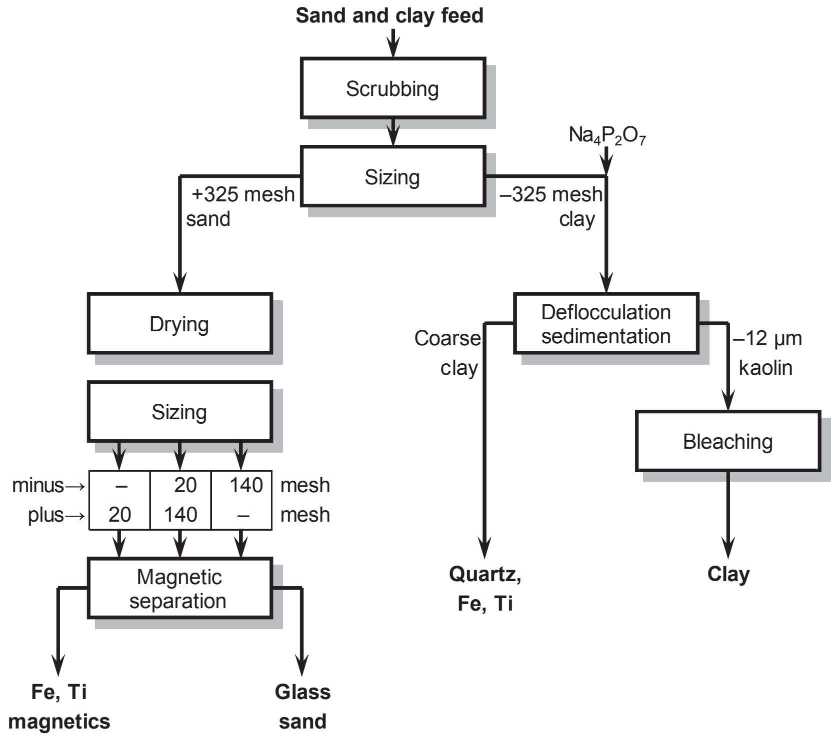

FIGURE 33.5

Flow sheet for separation of silica sand and kaolin clay.

Table 33.1 Chemical Composition of Silica Glass Sand

Element	The USA N. Jersey	The USA Illinois	The USA Oklahoma	The USA California	France	The UK
SiO_2	99.66	99.81	99.73	92.76	99.65	99.73
Fe_2O_3	0.025	0.017	0.020	0.127	0.02	0.013
Al_2O_3	0.143	0.055	0.090	3.799	0.08	0.057
TiO_2	0.027	0.015	0.012	0.034	–	–
CaO	0.007	<0.01	<0.01	0.060	–	–
MgO	0.004	<0.01	<0.01	0.017	–	–
K_2O	–	–	–	2.734	–	–
Na_2O	–	–	–	0.114	–	–
LOI	0.130	0.10	0.14	0.373	0.13	0.04

A plus 325-mesh fraction was dried followed by size classification. Each fraction was subjected to magnetic separation, where glass sand of over 99% SiO_2 was produced.

33.4 Chemical analyses of pure silica sand used for various applications

A large portion of silica is produced in the USA, the UK, France, and Canada using a process described in this chapter depending on impurities present in the ore body. Chemical composition of glass sand used in various applications is presented in Table 33.1.

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CHAPTER

Beneficiation of Barite Ores

34

CHAPTER OUTLINE

34.1 Introduction

This chapter deals with beneficiation of barite using the flotation method. Barite (or barytes meaning “heavy spar”) has an application as a weighting agent in the paper industry, paints, etc., and also for oil well drilling mud.

Production of barite dates back to the early 1930s, when only high-grade barite was mined (i.e., over 80% $BaSO_4$). The beneficiation method was exclusively washing, sizing, and gravity separation. Flotation studies were begun in the early 1950s, when barite flotation was carried out from a relatively complex ore and the physical separation method was not applicable.

Nowadays, a number of barite producers use flotation to recover barite from tailing dumps and complex ore that contains silica, fluorspar, calcite, celestite, and other impurities.

34.2 Barite ore deposits

Barite is the only barium mineral used in the production of $BaSO_4$ of various purities. Barite is not only produced from primary barite deposits, where barite is the primary mineral but there is a growing trend in processing the ores that contain barite in the

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form of gangue or as the secondary mineral. Deposits having barite is the primary mineral contain barite in a coarsely crystalline form. It has more or less an intergrown appearance when associated with other ores and minerals.

Mineralogically, barite is characterized by a rombic holohedral crystal system like other sulfides. The microstructure of $BaSO_4$ reveals almost regular tetrahedrons with O-atoms on the corners and the S-atom in the center. Barite crystals thus have an extremely symmetrical structure.

There are varieties of barite deposits from which barite is produced worldwide.

Deposits with barite replacements in limestone and argillite are found in the USA and eastern Europe. Similar formation deposits are contained in a bedded dark gray chart interbedded with carbonaceous, fossiliferous limestone lenses.

Vein deposits: These are different patterns of vein bedding replacement deposits. Some of these deposits contain fluorite and calcite with the interpenetrations and inclusions of barite into fluorite. Minor minerals include quartz celestite and iron oxide. Some of these deposits contain quartz, carbonates, iron oxide, and alumina as principle impurities.

Base metal deposits: There are a substantial number of sulfide base metal deposits containing copper, lead, zinc, pyrite, copper, and barite. The grade of barite in these deposits ranges from 20 to 45% $BaSO_4$. Barium from these deposits is recovered from sulfide tailings. Known deposits are located in Canada (British Columbia and Newfoundland), the USA, the Soviet Union, eastern Europe, and South America.

34.3 Beneficiation of barite ores

34.3.1 Synopsis

During the past 30 years extensive research work was performed on various barite ore types [1–4] using barite flotation methods, gravity preconcentration, and magnetic separation. Nowadays many operating plants are using the flotation methods to recover barite from complex ores. Processing methods for recovery of barite largely depend on the type of ore and gangue composition. Also, it depends on the liberation size of barite. When the barite liberation size is very fine, flotation is the preferred method. Barite ore is concentrated by either reverse or direct flotation. Reverse flotation generally involves removals of base metals sulfides or pyrite leaving a concentrated barite in the tailing, which is recovered using flotation. Direct flotation of barite is performed from the ores that contain fluorspar, silicates, and Rare Earth Oxides (REO). These ores are considered to be complex barite ores.

34.3.2 Beneficiation of barite ores using physical concentration method

The physical concentration method for recovery of barite is used with the ore that contains silicates, calcite, and iron as the principal gangue minerals. In the early 1960s, a number of operating plants used a combination of gravity concentration and magnetic separation. A generalized flow sheet is presented in Figure 34.1.

Using this flow sheet, a pharmaceutical grade of barium sulfate was produced assaying 97.5% $BaSO_4$, 0.0011% heavy metals, and 0.0001% Al_2O_3.

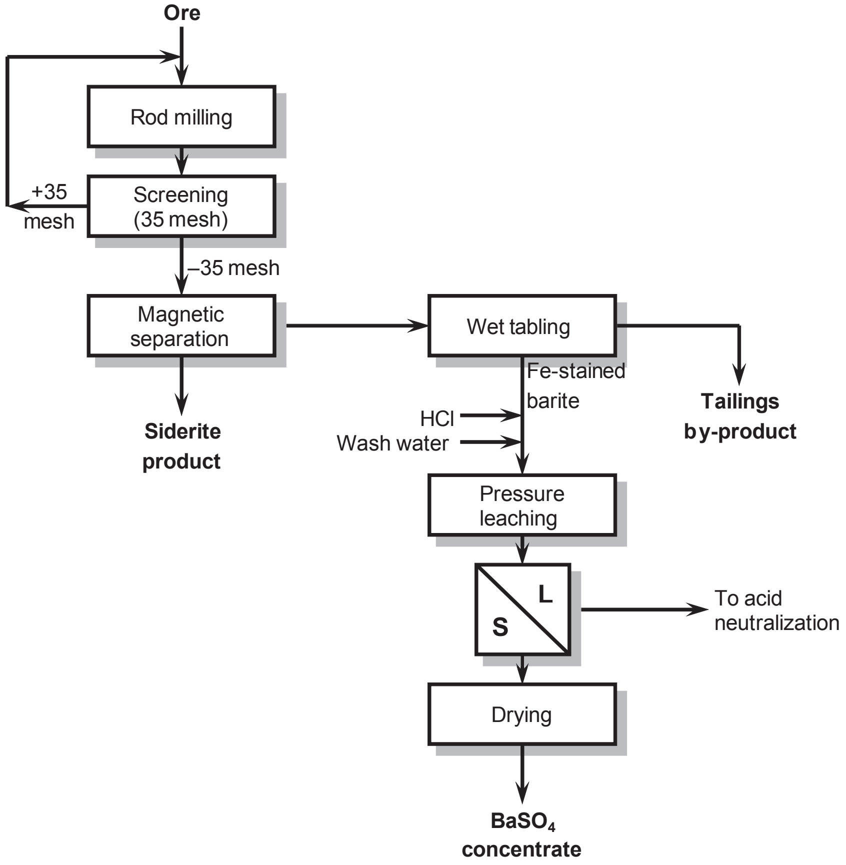

FIGURE 34.1

Generalized flow sheet for beneficiation of barite ores using magnetic separation gravity method.

Gravity concentrate produced was iron-stained. The concentrate was then leached using muriatic acid to remove iron.

Another treatment process involving a combination of gravity and flotation is shown in Figure 34.2. This was mountain concentrator (the USA). Using this flow sheet a chemical grade and drilling mud grade barite concentrate were produced.

Flotation was carried out using fatty acid at pH 8.5–9.0.

34.3.3 Beneficiation of barite ore that contains fluorspar and silica gangue minerals

There is little information on flotation of barite from the ores that contain fluorspar. Barite fluorspar ore usually contains other variable minerals such as REO. Known deposits are located in Vietnam and Canada. Two possible methods of beneficiation

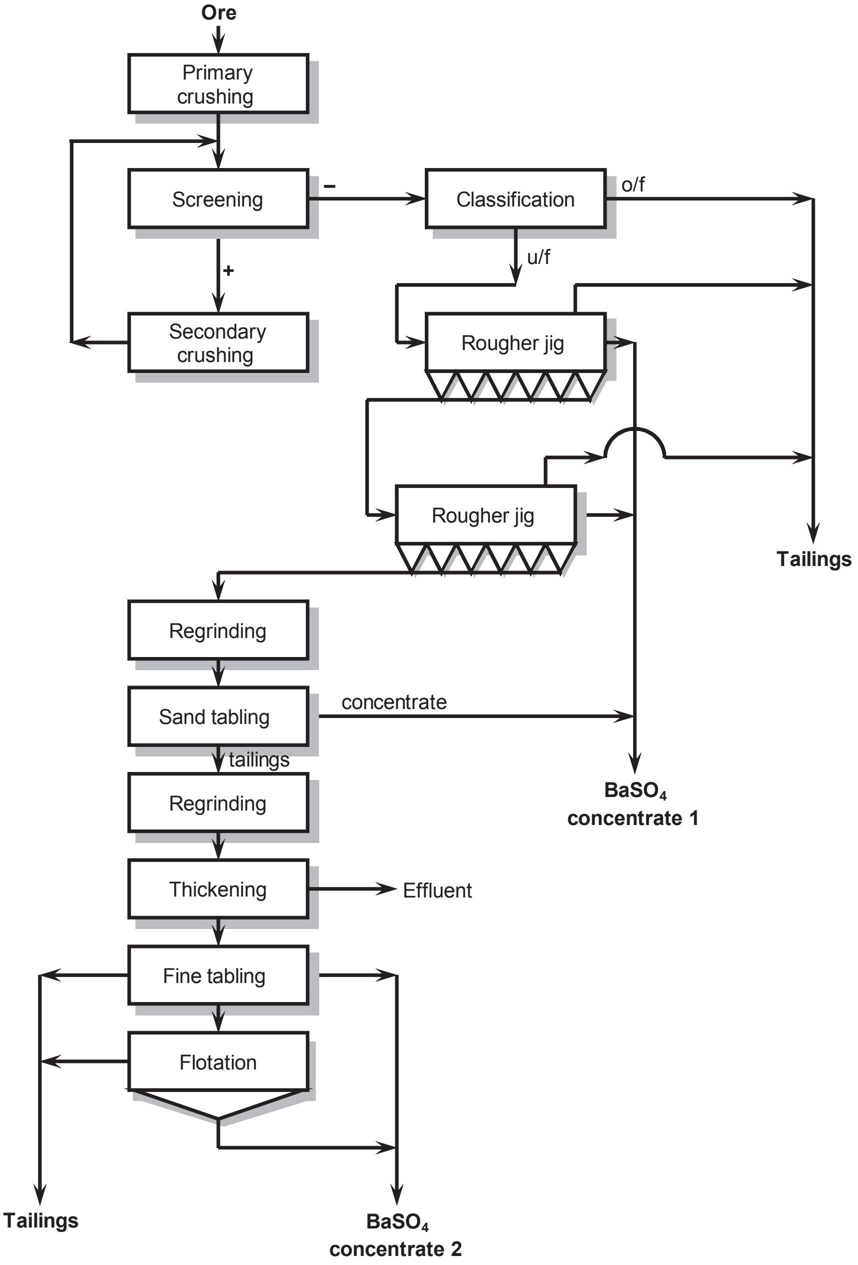

FIGURE 34.2

Flow sheet for beneficiation of barite using combinations of gravity and flotation.

of this ore were examined. These include (1) flotation of fluorspar ahead of barite flotation and (2) flotation of barite ahead of fluorspar flotation.

Sequential flotation of fluorspar–barite.

This testwork includes depression of barite using dextrin and quebracho and flotation of fluorspar ahead of barite. The conditions and results using this method are summarized in Table 34.1.

Although reasonably good CaF_2 grade was achieved, a large portion of fluorite reported to the barite concentrate was the main contaminates of the barite concentrate. Major improvement in the metallurgical results was achieved when floating barite ahead of fluorspar. Metallurgical results obtained by using this method are shown in Table 34.2.

When floating barite ahead of fluorspar, fluorspar does not float using a barite collector, which is the main attributing factor in achieving good selectivity.

A complex barite, fluorspar, rare earth oxide ore was treated to recover REO contained in a bastneasite and monazite mixture.

Table 34.1 Conditions and Results Obtained Using Sequential Fluorite Barite Flotation

(a) Conditions

	Additions g/t		**pH**	
Reagent	**CaF_2 Circuit**	**$BaSO_4$ Circuit**	**CaF_2**	**$BaSO_4$**
Depressants and Modifiers				
Corn dextrin	800–900	–	8.0	9.2
Quebracho	200–400	–		
Sodium silicate	800–950	600		
Citric acid	–	500		
Collector and Frother				
Amine acetate	300.0	–	8.0	9.2
Succinamide (R845)	–	420		
MIBC	–	25		

(b) Metallurgical Results

		Assays %		**% Distribution**	
Product	**Wt%**	**CaF_2**	**$BaSO_4$**	**CaF_2**	**$BaSO_4$**
CaF_2 cleaner concentration	17.94	94.05	0.85	75.0	0.5
$BaSO_4$ cleaner concentration	25.83	13.46	89.6	15.5	79.5
$BaSO_4$ rougher tail	56.23	3.82	10.34	9.5	20.0
Feed	100.00	22.5	29.1	100.0	100.0

Table 34.2 Continuous Locked Cycle Test Results Obtained Using Barite Flotation Followed by Fluorspar Flotation

		Assays %		% Distribution	
Product	**Wt%**	**CaF_2**	**$BaSO_4$**	**CaF_2**	**$BaSO_4$**
$BaSO_4$ cleaner concentration	29.62	0.9	95.8	1.2	94.6
CaF_2 cleaner concentration	21.26	96.9	0.3	92.8	0.2
$BaSO_4$ rougher tail	49.12	2.51	3.17	6.0	5.2
Feed	100.00	22.1	30.0	100.0	100.0

Selective flotation of REO in the presence of barite fluorite was poor. Also barite recovery was poor when using either sulfonate or fatty acid collector.

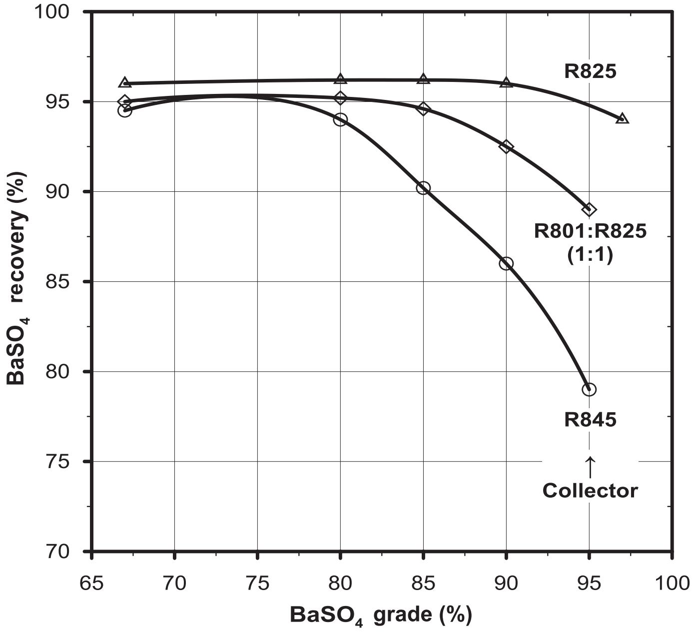

FIGURE 34.3

Effect of different barite collectors on barite grade recovery relationship.

In this research work a new highly efficient barite collector was developed. A new collector SR82 is composed of the mixture of petroleum sulfonate (R825), succinamate (R845), and alkyl sulfate in a ratio of 2:2:1. The effect of a new collector on barite grade recovery using complex $BaSO_4$, CaF_2 REO ore is illustrated in Figure 34.3.

Table 34.3 Continuous Test Results Obtained Using Barite Flotation Followed by Fluorspar Flotation Using a New Collector

		Assays %		% Distribution	
Product	**Wt%**	**CaF_2**	**$BaSO_4$**	**CaF_2**	**$BaSO_4$**
$BaSO_4$ cleaner concentration	61.75	0.55	96.8	5.5	97.2
CaF_2 cleaner concentration	5.80	82.2	1.3	77.0	1.2
CaF_2 flotation tail	32.45	3.34	0.3	17.5	1.6
Feed	100.00	6.20	61.5	100.0	

The metallurgical results obtained in a continuous test are shown in Table 34.3.

These data have demonstrated that the new collector is a highly effective barite collector.

34.4 Research and development

A large portion of development testwork was performed on complex barite containing ores mainly from secondary sources derived from base metal and sulfide ores that contain barite. Studies were also conducted on the ores that contain fluorspar, albite, and mica minerals.

34.4.1 Collector choice

A fair amount of research work was devoted to examination of various fatty acids [5,6] on barite flotation from different ore types. Neither fatty acid nor tall oils has found industrial application due to the fact that using fatty acids selectivity between barite and gangue minerals was not satisfactory. If the ore contains calcite and fluorspar, using tall oil, both calcite and fluorspar report to the barite concentrate. Reasonably good results with oleic acid were achieved on the ores that contain silica as gangue minerals [7]. Figure 34.4 shows the efficiency of pH on barite flotation using oleic acid.

In an extensive research conducted during the 1980s, a series of different collectors were examined [8,9]. In this research, a sulfide flotation tailing that contains about 40% barite was used.

The collector type is tested and the metallurgical results are presented in Table 34.4.

In these tests pH was maintained at 8.5 with sodium carbonate. The depressant used was sodium silicate at 900 g/t. Barium chloride was used as an activator at a dosage of 300 g/t.

From the data generated, succinamate collectors and a new collector mixture RS82 gave the best metallurgical results.

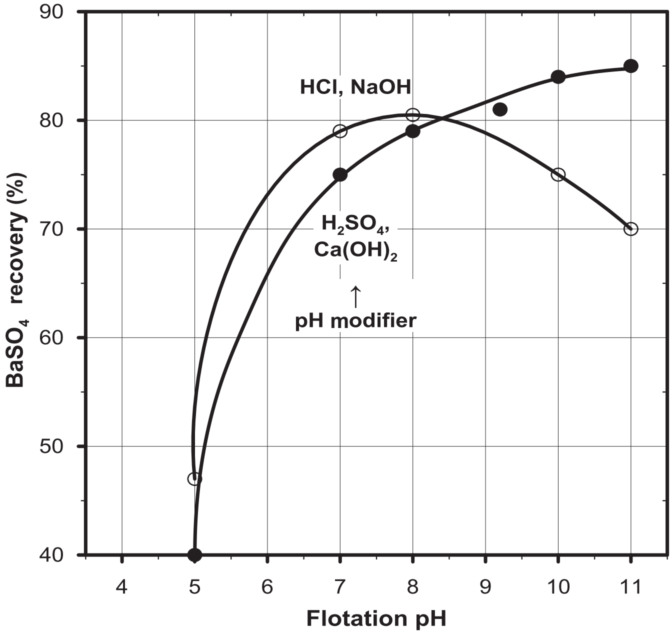

FIGURE 34.4

Effect of pH on barite flotation from siliceous ore using oleic acid.

Table 34.4 The Effect of Different Collectors on Barite Flotation from Sulfide Tailing

		Barite Concentrate	
Reagent Type	**Collector Additions g/t**	**Grade % $BaSO_4$**	**Recovery % $BaSO_4$**
Sodium fatty alcohol sulfate	700	88.5	79.3
Sodium tallow fatty alcohol sulfate	700	90.1	85.5
Sodium coconut alkyl sulfosuccinamate	700	94.3	90.2
Sodium alkyl sulfosuccinamate	700	95.5	93.3
Sodium fatty alcohol ether sulfate	700	89.3	80.5
Petroleum sulfonate (Cytec R825)	700	91.5	89.6
Petroleum sulfonate (Cytec R801)	700	93.1	91.0
Alkyl succinamate (Cytec R845)	700	95.5	94.4
Collector SR82	500	98.6	98.4

Table 34.5 The Effect of Collector RS82 on Barite Flotation from Sulfide Tailings

			Assays %				Recovery %
Operation	**Product**	**Wt%**	**$BaSO_4$**	**Fe_2O_3**	**Al_2O_3**	**SiO_2**	**$BaSO_4$**
Milpo Peru	$BaSO_4$ Cl concentration	28.04	98.4	0.01	0.02	0.1	97.5
Cerro Lindo	$BaSO_4$ tails	71.96	0.98	–	–	–	2.5
Zn tail	Feed	100.0	28.3	–	–	–	100.0
BC Canada	$BaSO_4$ Cl concentration	19.66	97.6	0.02	0.04	0.2	96.9
Lead tail	$BaSO_4$ tails	80.35	0.76	–	–	–	3.1
	Feed	100.0	19.8	–	–	–	100.0

The new RS82 collector was tested on several sulfide tailings. The results obtained are shown in Table 34.5.

From the data generated it has been demonstrated that the new collector mixture gave excellent barite metallurgical results.

34.4.2 Modifying reagents

The modifying reagents normally used during barite flotation are listed in Table 34.6.

Soda ash is usually used during barite flotation to maintain pH at 8–10, which depends on the type of collector used. An alternative to soda ash is sodium hydroxide, which is used when little or no calcite is present in the barite flotation feed.

Sodium silicate is an important reagent during barite flotation. It acts as a dispersant and silicate depressant. Dosages usually range from 500 to 2000 g/t.

The effect of sodium silicate on barite flotation using different collectors is illustrated in Figure 34.5.

Aluminum chlorite studies have shown that in the presence of aluminum chlorite, depression of calcite is improved at dosages of about 300 g/t. Higher additions have a negative effect on barite flotation.

Quebracho is a major calcite depressant during barite flotation from the ore that contains calcite. Higher dosages over 400 g/t may have a negative effect on barite recovery.

Citric acid is a fluorspar depressant and is used during barite flotation from the ores that contain fluorspar. It is used when barite is floated ahead of fluorspar. Dosages of 300–800 g/t are used. The effect of citric acid on barite and fluorspar flotation is illustrated in Figure 34.6.

Good depression of fluorspar was achieved with the addition of citric acid above 500 g/t.

Table 34.6 Modifying Reagents Used during Barite Flotation

Reagent	Function
Soda ash (Na_2CO_3)	pH modifier, quartz depressant
Sodium silicate	Silica depressant, slime dispersant
Aluminum chlorite ($AlCl_3$)	Calcite depressant
Quebracho	Calcite depressant
Citric acid	Fluorite depressant
Tanic acid	Calcite depressant
Oxalic acid	Silica and iron oxides depressant
Sodium fluoride (NaF)	Barite depressant
Barium chloride ($BaCl_2$)	Barite activator

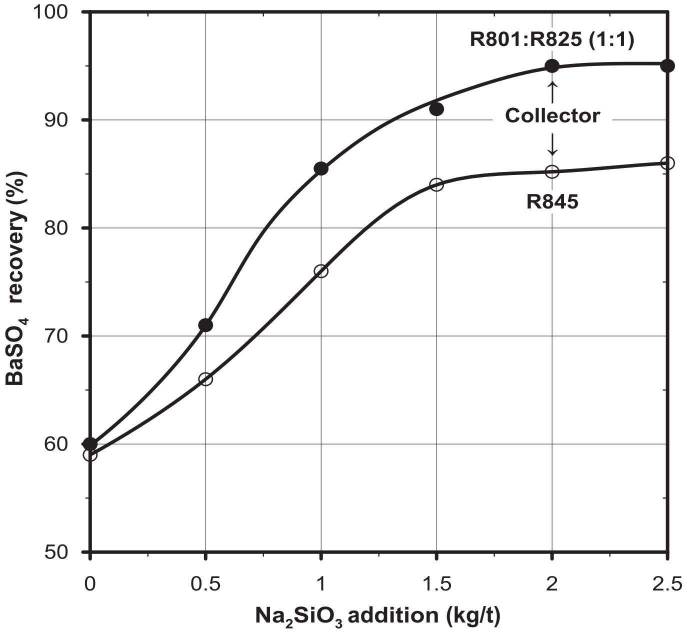

FIGURE 34.5

The effect of sodium silicate on barite flotation.

Tanic acid is also a calcite depressant and sometimes is used together with quebracho during barite flotation.

Oxalic acid is used for silica depression during barite flotation from siliceous ore. It is also used as a mixture of citric and oxalic acid for depression of feldspar.

Sodium fluoride (NaF) is a barite depressant and is used during beneficiation of barite, fluorspar ore when fluorspar is floated ahead of barite.

Another barite depressant is $FeCl_3$ in the presence of tall oil as fluorspar collector.

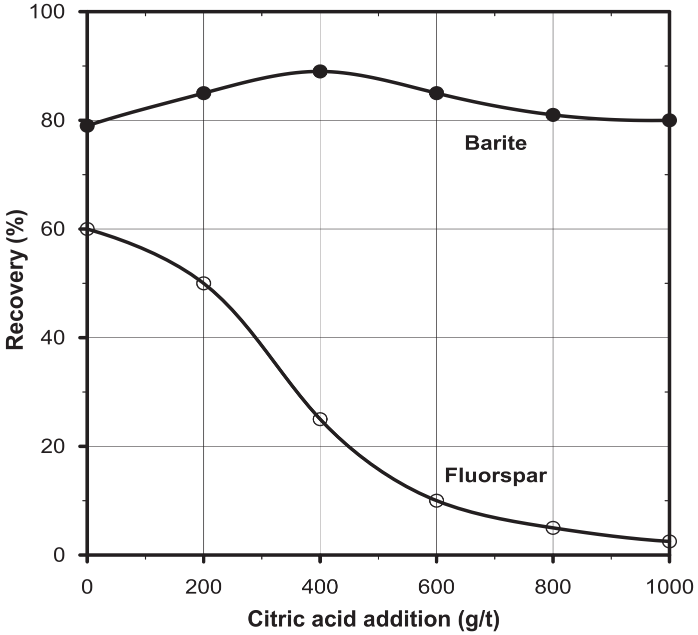

FIGURE 34.6

The effect of citric acid on barite–fluorspar separation using collector mixture R801:R825 (1:1).

34.4.3 Activating reagents

In the research studies a number of barite activating inorganic agents were examined [10]. This includes NaCl, $MgCl_2$, $Pb(NO_3)_2$, and $BaCl_2$. From the testwork the following conclusions have been made:

- NaCl and $MgCl_2$ had a depressing effect on both barite and fluorspar.
- $BaCl_2$ and $Pb(NO_3)_2$ both have an activating effect on barite, while $BaCl_3$ had a depressing effect on fluorspar.
- The effect of $BaCl_2$ and $Pb(NO_3)_2$ on barite flotation is illustrated in Figure 34.7.

In these experiments, collector R845 (succinamate) was used. In the operating plants $BaCl_2$ was the standard activator used.

34.5 Specification for commercial barite products

The barite market is divided into three different product grades as (1) drilling mud, (2) chemical grade, and (3) filler grade. Typical specification of these products is shown in Table 34.7.

A specific requirement is the product having an $SrSO_4$ content below 2%.

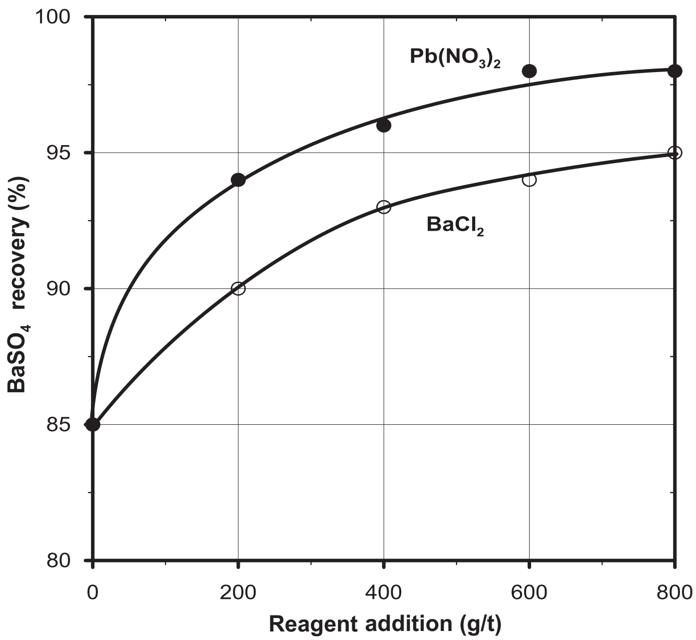

FIGURE 34.7

The effect of $BaCl_2$ and $Pb(NO_3)_2$ on barite flotation.

Table 34.7 Typical Specification of Commercial Barite Products

Drilling Mud	Chemical Grade	Filler Grade
$BaSO_4$ = >92% Specific gravity = 4.2 g/cm^3 % 0.075 mm = <989% % 0.006 mm = >70%	$BaSO_4$ = >96–98% CaF_2 <0.5% SiO_2 <1.0% F_2O_3 = 0.5% $SrSO_4$ = <2% Sr/Bo = <0.017 100% < 0.04 mm	$BaSO_4$ = >85–95% Brightness = 70–95% 100% < 0.045 m

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CHAPTER

Beneficiation of Celestite Ores

35

CHAPTER OUTLINE

35.1 Introduction

Celestite resources are widely spread in Canada, the USA, China, as well as other countries. Until recently, strontium was one of the less important elements from the viewpoint of volume of production. The situation has been changed, however, by the recent discovery of two major uses of strontium. Firstly, strontium is suitable for use as an absorber in color television tubes to reduce the intensity of X-ray radiation and secondly, it is the basic raw material used in the manufacture of ceramic permanent magnets.

Initially the beneficiation of celestite ore was mainly physical concentration involving gravity, magnetic separation, and in some cases heavy liquid separation. Nowadays flotation becomes the most efficient way for the production of high-grade celestite.

35.2 Celestite ore deposits

Celestite ($SrSO_4$) is the main strontium mineral. It has a hardness of 3–3.5 and specific gravity of 3.96. Celestite occurs mainly in sedimentary deposits associated with rock salt and gypsum. In these deposits celestite is the major mineral ranging from

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00035-X

70 to over 90% $SrSO_4$. In some deposits barium is present in small amounts usually in solid solution with celestite.

Some deposits from Canada (i.e., Nova Scotia) contain barite and calcite with a minor amount of pyrite. Deposits in the Ontario region are essentially composed of fluorite and celestite with a complex variety of minor minerals, including quartz, feldspar, and apatite with some base metal sulfides.

The major world celestite deposits are located in Canada, China, Russia, and the USA.

35.3 Beneficiation of celestite ore

There are two basic methods for beneficiation of celestite ore. They are: (1) physical concentration and (2) flotation.

Physical concentration, which includes gravity and heavy liquid separation, is practiced on relatively high-grade ore that contains calcite and silicate. Nowadays flotation is the principal method in beneficiation of celestite ore.

35.3.1 Gravity preconcentration

In the early days before development of the flotation technique, celestite was beneficiated using either gravity preconcentration or heavy liquid separation.

High-grade celestite concentrate using gravity concentration can be achieved on relatively coarse-grained ore that contains clay, calcite, and limonite. A typical plant flow sheet using gravity preconcentration [1] is shown in Figure 35.1.

The flow sheet is designed in such a way to remove clay and limonite using attrition tumbler and washer.

In the gravity circuit, a concentrate grade ranging from 98 to 93% $SrSO_4$ is usually produced with the recovery of about 85–88% $SrSO_4$. The highest concentrate grade is achieved on coarser fractions (i.e., 97% $SrSO_4$).

35.3.2 Flotation research and development

35.3.2.1 Collector choice

Although alkaline salts of oleic acid, in particular, sodium oleate were extensively examined [2] by Russian researchers, these collectors did not find application in practice due to poor selectivity toward gangue minerals, in particular, calcite.

Using a calcite depressant, such as quebracho and sodium silicate during celestite flotation, and using sodium oleate [3], both celestite and calcite were completely depressed.

In the other studies [4], collectors such as *n*-alkylammonium chloride, sodium *n*-alkyl sulfonate, and sodium dodecyl sulfate were examined. Using these collectors the recovery of celestite was a function of pH. The highest recovery was achieved

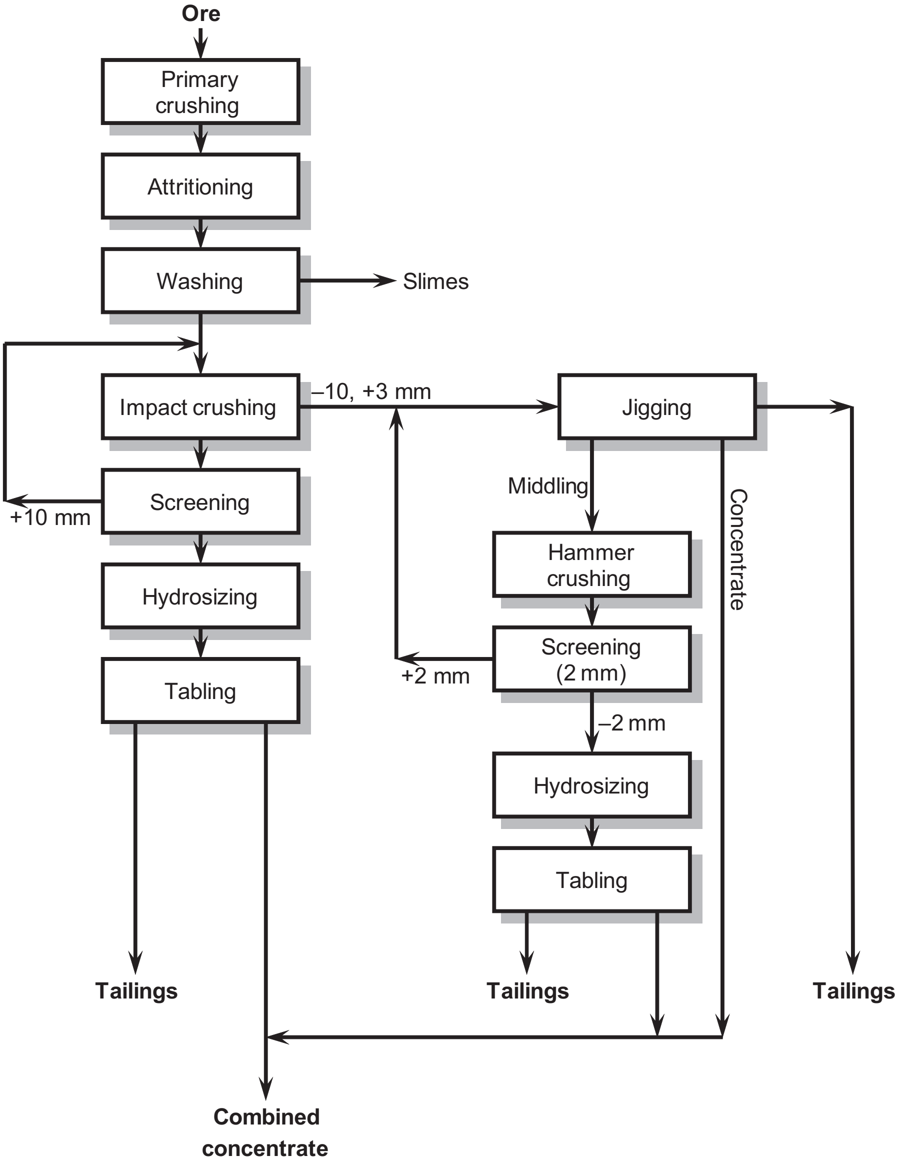

FIGURE 35.1

Flow sheet used in gravity preconcentration.

between pH 7 and 9. At pH above 9.0, celestite recovery drops sharply. Figure 35.2 shows the effect of pH on flotation recovery of celestite.

Other collectors examined on various ores include alkyl sulfosuccinamate (SAM), alkyl succinamate (R845), and sodium oleil tartarate (Igepal T33). In these

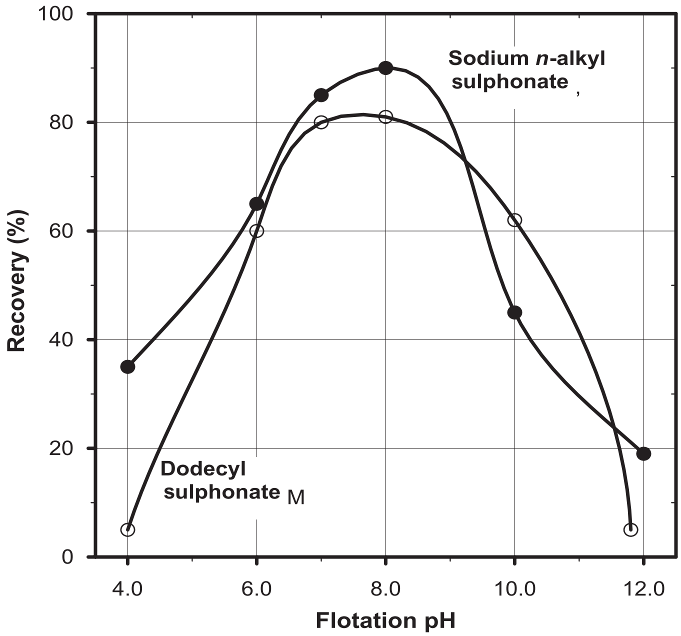

FIGURE 35.2

The effect of pH on flotation of celestite using collectors: dodecyl sulfate and sodium *n*-alkyl sulfonate.

Table 35.1 Flotation Test Results Obtained with Different Collectors

Collector	Additions g/t	Assays			% Distribution
		$SrSO_4$	$BaSO_4$	SiO_2	$SrSO_4$
Alkyl sulfosuccinamate	100	97.2	1.2	0.5	75.0
	200	96.0	1.3	0.8	88.0
	400	95.5	1.3	1.1	93.4
Alkyl succinamate R845	100	98.0	1.1	0.4	77.0
	200	97.0	1.2	0.6	90.2
	400	96.0	1.3	0.8	94.0
Sodium oleil tartarate igepon T33	100	96.0	1.4	1.1	65.5
	200	95.1	1.5	1.4	75.8
	400	93.3	1.0	1.8	82.9

experiments, ore assaying 75–85% $SrSO_4$ was used. The results obtained with different levels of these collectors are summarized in Table 35.1. In these tests oxalic acid and sodium silicate were used as calcite and silica depressants.

Collectors SAM and R845 performed well. Using these collectors, good $SrSO_4$ grade and recovery were achieved. Collector T33 was not as efficient.

35.3.2.2 Depressant choice

No significant data on the selection of depressants exist in the literature. In most recent studies [4,5], various depressant combinations were examined on the ores that contain calcite, silica, and clay. A combination of sodium silicate and oxalic acid has been shown to depress calcite and silica minerals. However, higher additions of sodium silicate tend to depress celestite. Figure 35.3 shows the effect of the level of sodium silicate on celestite flotation using different collectors.

Using oleic acid a sharp drop in celestite recovery was evident with an increase in sodium silicate addition.

35.3.2.3 Modifiers

During celestite flotation, pH is maintained between 7 and 9. The pH modifiers used are soda ash (Na_2CO_3) or sodium hydroxide (NaOH). In most of cases soda ash performed much better than sodium hydroxide. Figure 35.4 shows grade recovery relationship using two pH modifiers.

In these experiments, the flotation pH is maintained at 8.0.

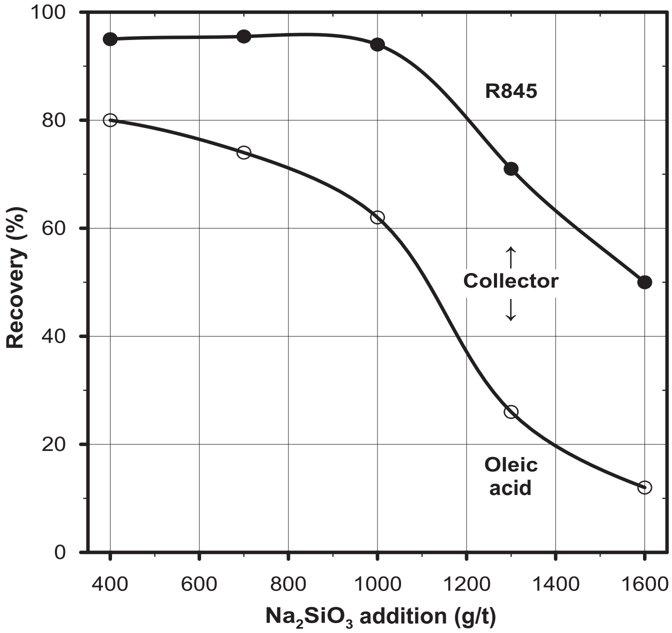

FIGURE 35.3

The effect of levels of sodium silicate on celestite flotation.

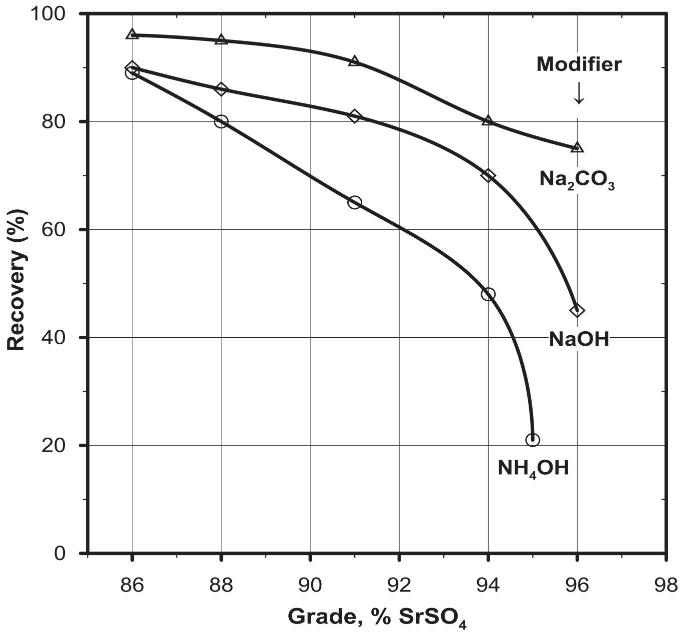

FIGURE 35.4

Celestite grade recovery relationship using different pH modifiers.

35.3.3 Practical flotation system

Because of the frequent occurrence of silicates calcite and clay in the celestite ore, a succinamate collector is generally favored for celestite flotation. The use of a mixture of frother acid and oleic acid as a froth extender improves celestite recovery without affecting concentrate grade.

During celestite flotation sodium silicate was used for silica depressant and slime dispersant. Oxalic acid is used for a calcite depressant. If the fluorite is present in the ore oxalic acid may be replaced with citric acid.

In a number of cases sulfides and base metals are present in the ore in which case pyrite or base metals are removed ahead of celestite flotation.

35.3.3.1 Beneficiation of celestite ore containing fluorite and silica

The ore from British Columbia, Birch Island (Canada), is beneficiated using a reagent scheme shown in Table 35.2. Metallurgical results obtained are shown in Table 35.3.

Good metallurgical results were achieved using the reagent scheme shown in Table 35.2.

In this development testwork, the flotation extender MIBC/fatty acid mixture was studied in more detail. The effect of the level of MIBC/fatty acid mixture is shown in Figure 35.5. The data shown in the figure have demonstrated that the mixture improved $SrSO_4$ recovery without losses in concentrate grade.

Table 35.2 Reagent Scheme Used in Beneficiation of Fluorite—Celestite Ore

	Additions g/t		
	Conditioning + Rougher	**Cleaners**	**pH**
Depressant and modifiers			
Soda ash (Na_2CO_3)	900		7.5
Citric acid	600	200	
Sodium silicate	700	200	
Collectors and frothers			
R845 (succinamate)	200	50	7.5
Methyl Izobutyl Carbanol (MIBC):fatty acid (1:1)	150	20	

Table 35.3 Celestite Flotation Results Obtained in a Continuous Locked Cycle Test

		Assays %					% Distribution
Product	**Wt%**	**$SrSO_4$**	**$BaSO_4$**	**CaO**	**MgO**	**SiO_2**	**$SrSO_4$**
$SrSO_4$ Cl concentration	20.56	94.5	2.30	0.95	0.40	0.35	88.3
$SrSO_4$ tailings	79.44	3.24	–	–	–	–	11.7
Feed	100.00	22.0	–	–	–	–	100.0

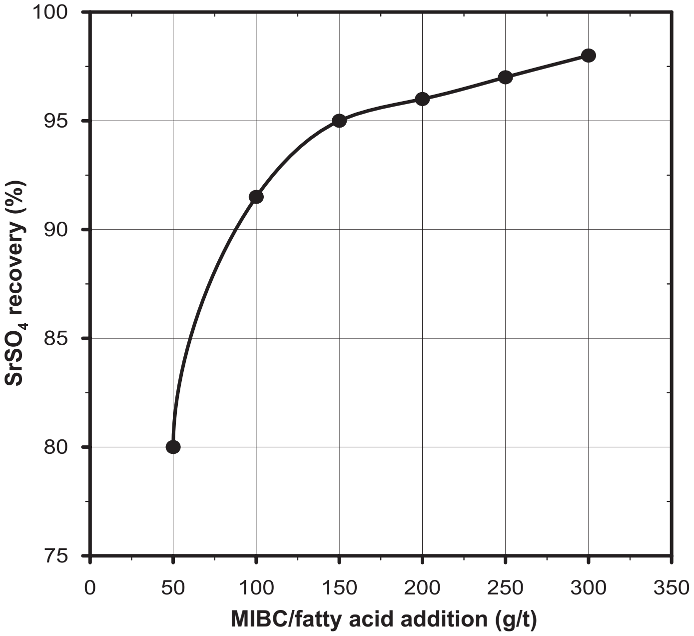

FIGURE 35.5

The effect of mixture MIBC/fatty acid ratio (1:1) on celestite recovery.

35.3.3.2 Beneficiation of celestite ore from sulfide tailing

The celestite ore containing sulfides usually contains silica clay acid calcite as a major gangue mineral. Flotation response of celestite from this ore is somewhat different from that of celestite from the ore that contains fluorspar. Flotability of celestite from this type of ore depends on the type of depressant used as well as on the type of collector. A typical example of the reagent scheme used for treatment of such an ore is shown in Table 35.4.

The depressant A-2 is a mixture of sodium silicate and aluminum sulfate in a ratio of 3:1.

Metallurgical results obtained in a continuous operation are shown in Table 35.5. Depressant A-2 was much more effective than sodium silicate along.

Table 35.4 Reagent Scheme Used in Beneficiation of Celestite from Sulfide Tailing

	Reagent Additions g/t			
Reagents	**Sulphates Flotation**	**$SrSO_4$ Rougher**	**$SrSO_4$ Cleaner**	**pH**
Depressants and modifiers				
Soda ash	–	300	150	7.8
Depressant A-2	–	600	400	
Oxalic acid	–	300	200	
Collectors and frothers				
Alkylsulfosuccinamate	–	200	100	7.8
Amil xanthate	20	–	–	
MIBC:oleic acid (1:1)	–	50	30	

Table 35.5 Metallurgical Results Obtained in a Locked Cycle Test Using Reagent Scheme from Table 35.4

		Assays %					**% Distribution**
Product	**Wt%**	**$SrSO_4$**	**$BaSO_4$**	**CaO**	**MgO**	**SiO_2**	**$SrSO_4$**
$SrSO_4$ cleaner concentrate	54.78	97.8	1.80	0.45	0.30	0.25	93.5
$SrSO_4$ flotation tail	40.22	7.33	–	–	–	–	5.2
Sulfide concentration	1.50	4.40	–	–	–	–	0.0
Slimes	3.50	20.3	–	–	–	–	1.3
Feed	100.00	57.3	–	–	–	–	100.0

35.4 Celestite uses and specifications

Celestite is used in the following areas:

- For manufacture of strontium carbonate and strontium nitrate
- For production of strontium metal
- For glass manufacture
- For electronics industry

Strontium specification for production of strontium carbonate and strontium nitrate is shown in Table 35.6

Table 35.6 Celestite Concentrate Specification for Production of Strontium Carbonate and Strontium Nitrate Production

Element	% Assays	
	For Strontium Carbonate $Sr(CO_3)_2$	For Strontium Nitrate $Sr(NO_3)_2$
$SrSO_4$	90–95	95 min
$BaSO_4$	1–2	2 max
SiO_2	1–2	n/a
Fe_2O_3	0.4–0.5	n/a
PbO	Low	n/a
F	0.1 max	n/a
$CaSO_4$	2.0	1.5 max
$CaCO_3$	0.5	1.5 max
Free moisture	2.0 max	1.5 max

Table 35.7 Strontium Carbonate Specification for Metal ,Glass and Electronics is shown in Table 35.7

Element	Assays %		
	Metal	Glass	Electronics
$SrCO_3$	99.0 min	96.0 min	96.0 min
$BaCO_3$	0 max	3.0 max	1.5 max
$CaCO_3$	0.2 max	0.5 max	n/a
$MgCO_3$	0.2 max	n/a	n/a
Na_2CO_3	0.15 max	1.0 max	n/a
SO_2	0.08 max	0.4 max	0.4 max
Fe_2O_3	0.01 max	0.01 max	n/a

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CHAPTER

Beneficiation of Potash Ore

36

CHAPTER OUTLINE

36.1 Introduction

Potash, the common name for potassium compounds, is also used frequently to indicate potassium oxide (K_2O) equivalent of a compound, even though the compound may contain no oxide. For example, the chief compound of potassium in most potash ores is potassium chloride (KCl), while concentrates are sold on the basis of equivalent K_2O content (about 60% for muriate).

The potassium salts may be obtained from the following sources:

1. Solid deposits of soluble potassium minerals such as sylvite, carnalite, kainite, etc.
2. Seawater and salt lake deposits or brines
3. Vegetable substances such as wood, ashes, sugar, beet residue, etc.
4. Animal material such as wool washings.
5. Insoluble potash-bearing minerals such as alunite, feldspar, leucite, muscovite, etc.

The greater part of the world supply of potash is obtained from solid deposits of soluble potassium minerals from Group 1.

The potash minerals occurring in these deposits are all soluble in water and it is easy to concentrate their solutions to a high percentage of potassium oxides.

This chapter deals with the beneficiation of the potash ores from solid deposits.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00036-1

Table 36.1 List of Soluble Potash Minerals Found in Various Solid Deposits

Mineral	Formula	% Potash Calculated as K_2O
Carmallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	16.9
Douglasite	$2(KCl \cdot H_2O) \cdot FeCl_2$	32.2
Glasserite	$3K_2SO_4 \cdot Na_2SO_4$	37.5
Hartsal	$NaCl \cdot KCl \cdot MgSO_4 \cdot H_2O$	13.9
Kainite	$MgSO_4 \cdot KCl \cdot 3H_2O$	18.9
Kaliborite	$KMg_2B_{11}O_{19} \cdot 9H_2O$	7.5
Krugite	$KSO_4 \cdot MgSO_4 \cdot 4CaSO_4 \cdot 2H_2O$	10.8
Langbeinite	$2\ MgSO_4 \cdot K_2SO_4$	22.7
Leonite	$K_2SO_4 \cdot\ MgSO_4 \cdot 4H_2O$	23.3
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$	15.6
Rinneite	$FeCl_3 \cdot 3KCl \cdot NaCl$	34.7
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	23.5
Sylvinite	$NaCl \cdot KCl$ (mechanical mix)	30.2
Sylrite	KCl	63.2
Syngenite	$CaSO_4 \cdot K_2SO_4 \cdot H_2O$	28.8

36.2 Potash deposits and minerals

Potash solid deposits are wide spread around the world. Major deposits are located in Germany, France, Spain, Russia, and Canada. Canadian deposits are the world's largest deposits and are located in the province of Saskatchewan, New Brunswick, Quebec, and Ontario.

The main minerals present in the solid deposits are listed in Table 36.1.

The potash salts in most of the major world deposits are closely associated with beds of halite (sodium chlorite ore, common salts).

Some of the deposits found in Ontario belong to the middle Jurassic and include deltaic sandstones shale (including the well-known alum shale and jet rocks).

In the other ore body potash deposits occur in the open portion of evaporite formation.

Nevertheless, the most important potash ore is sylvinite, a mixture of sylvite (KCl) and halite (NaCl) with minor amounts of clay and other potassium minerals.

36.3 Beneficiation of potash-containing ores

36.3.1 General

Nowadays, the majority of the sylvinite ores in the world are concentrated by froth flotation involving brines.

A number of features [1,2] make potash ore flotation different from any other conventional flotation process. Since these are water-soluble salts, flotation is carried out in saturated brine, a highly concentrated electrolyte system (about 6 mol/L KCl + NaCl brine saturated at 20 °C). The properties of an aqueous system at such a high electrolyte concentration are very different from dilute aqueous solution employed in conventional flotation processes. The high concentration of ions, which actively interact with water (hydration), affects all processes that take place in such a system and renders some minerals floatable. For example [3] as collector concentration exceeds critical micelle concentration, the mineral flotability rapidly decreases in a conventional flotation system; on the other hand, no flotation of sylvite is obtained until precipitation of amine (common sylvite collector) occurs in the solution.

36.3.2 Flotation properties of sylvite and halite

Studies were carried out on sylvite and halite flotation using dodecylamine hydrochloride and sodium louvate collectors [4,5].

It is shown that KCl floats well with amine ($R_{12}NH_3Cl$) while NaCl is depressed. Figure 36.1, shows flotation recovery of KCl and NaCl as a function of dodecylamine hydrochloride concentration.

It was postulated that NaCl did not float due to the fact that the positively charged $R_{12}NH_3Cl(s)$ has the same charge as NaCl. The carboxylate collector is negatively charged and does not adsorb on negatively charged NaCL, where in this case,

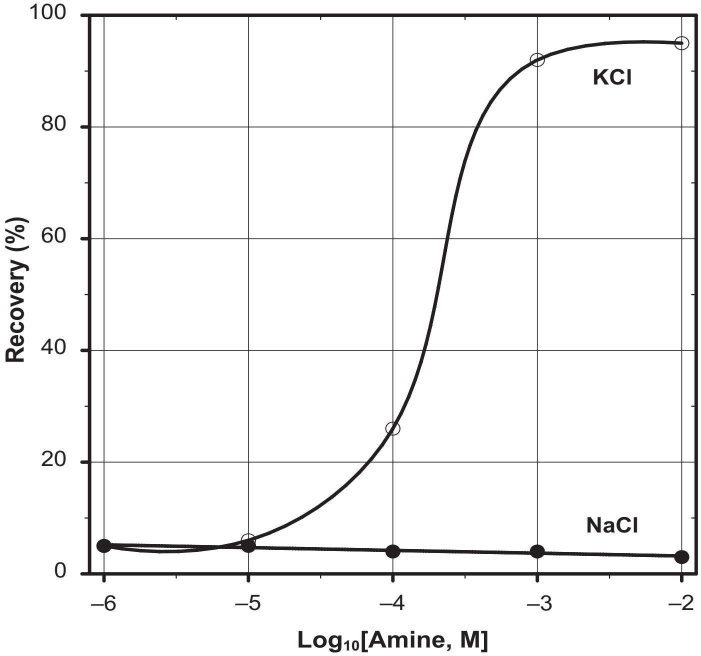

FIGURE 36.1

The effect of dodecylamine hydrochloride concentration on KCl and NaCl flotation recovery.

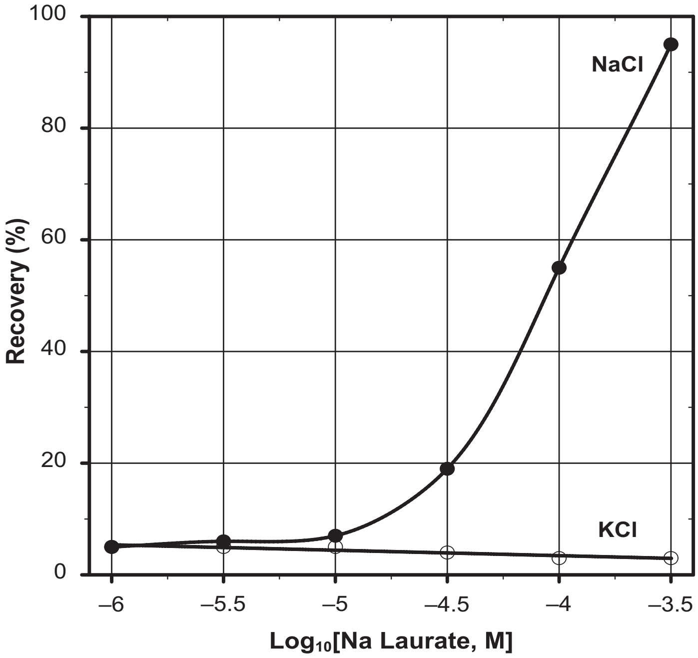

FIGURE 36.2

The effect of sodium laurate concentration on flotation recovery of NaCl and KCl.

positively charged NaCl floats while KCl is depressed. As an example, the effect of sodium laurate concentration on NaCl and KCl is illustrated in Figure 36.2.

It should be noted that in the use of ultrasonic collector dispersion techniques, the flotation recovery of NaCl or KCl increases significantly.

The flotation results for KCl and NaCl clearly indicated that dispersion of collector colloids and subsequent flotation of these salts are related to the surface charge of the collector colloid and the surface charge of the alkali halide particles.

There are a number of amine and sulfonate collectors used for potash salt flotation. Table 36.2 shows the collectors that are successfully used for potash mineral flotation.

From the experimental testwork conducted with these collectors [6], the following have been concluded:

- Dodecyl and tetradecyl chloride float KCl well at a concentration of 10^{-4} mol/L.
- Octylamine floats KCl well at a concentration above 10^{-4} mol/L while NaCl is depressed.
- Sulfonate collectors float KCl at a relatively high concentration.
- Caprylic acid floats NaCl well while KCl is depressed.

Table 36.2 List of the Collectors Used in Potash Minerals Flotation

Collector	Purity %
Octylamine	97.8
Dodecylamine chloride	99.0
Tetradecylamine chloride	99.0
Hexadecylamine chloride	99.0
Caprylic acid	99.0
Sodium octyl sulfonate	87.0
Sodium dodecyl sulfonate	96.9

36.4 Treatment of potash ore in the presence of insoluble slimes

The presence of insoluble slimes in potash ores is a processing problem of some significance to the potash industries. These insolubles must be removed prior to potash flotation due to their high adsorptive capacity for amines, which are used as potash flotation collectors. Sylvinites may contain up to 15% insoluble gangue minerals. Usually these are sulfates, carbonates, iron oxides, and clay minerals.

There are several methods used for slimes removal. These include:

1. Mechanical desliming
2. Flocculation flotation and desliming
3. Flocculation flotation followed by sylvite flotation.
    a. *Mechanical desliming* is accomplished in a cyclone (Figure 36.3) after scrubbing. After primary slime removal the cyclone underflow is sized followed by flotation.

Another method reported in the literature [7] was the use of sparge cyclone slime flotation, which was developed in the early 1980s.

- Flocculation–flotation and desliming method involves scrubbing, sizing, and desliming. The slimes are conditioned with flocculent and collector followed by slime flotation. The slime tailing and coarse fraction are subjected to potash flotation. The flow sheet using this process is presented in Figure 36.4.

It should be pointed out that during potash flotation from slime tailing, depressants such as dextrin or guar gum are used.

- Flocculation–flotation is followed by sylvite flotation method, scrubbing, conditioning, sizing, and sylvite flotation. A generalized flow sheet using this method is presented in Figure 36.5. This method involves, scrubbing, conditioning followed by slime flotation. Slime tailing is classified followed by sylvite flotation.

Another method for slimes removal involves the use of magnetite and flocculation [8]. This principle has been applied to enhance the magnetic response of the

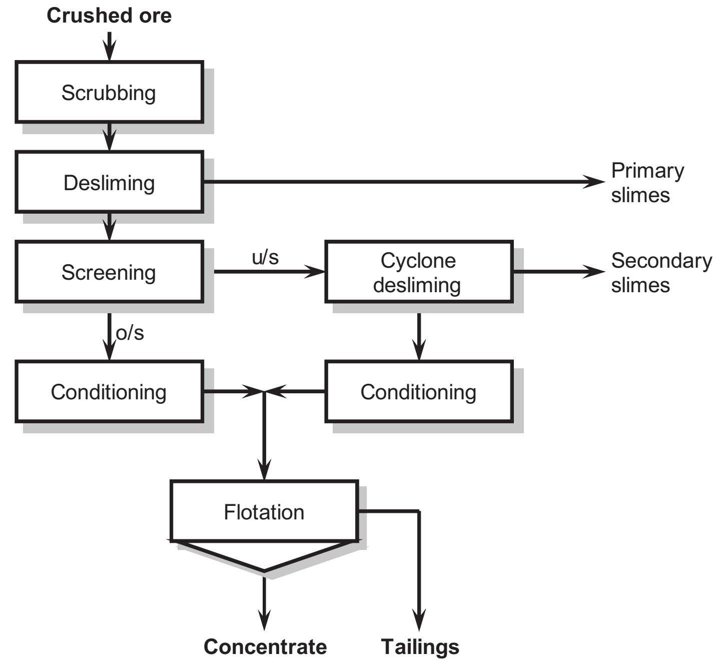

FIGURE 36.3

Simplified flow sheet of potash flotation using cyclone desliming.

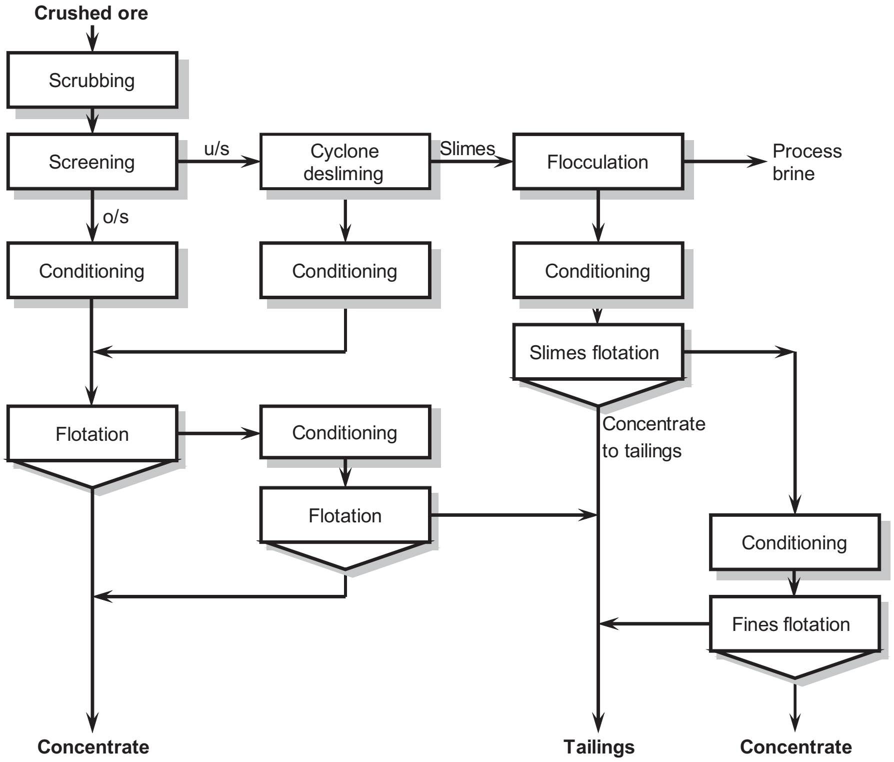

FIGURE 36.4

Flow sheet that includes flocculation–flotation desliming.

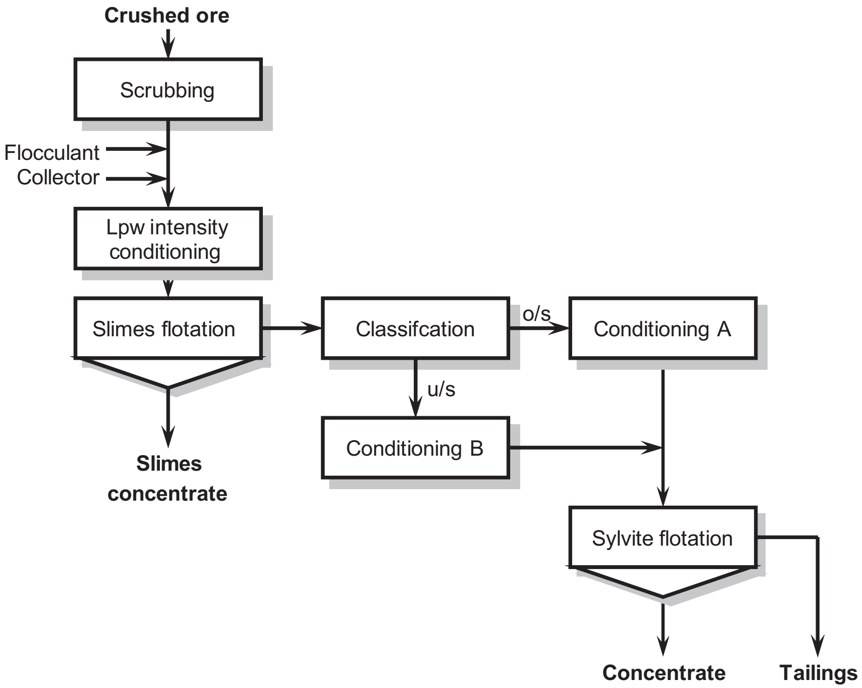

FIGURE 36.5

Flow sheet showing the flocculation flotation classification followed by sylvite flotation.

Table 36.3 Metallurgical Balance Using Magnetite–Flocculant for Insoluble Slime Removal

		Assays, %				% Distribution			
Product	**Wt%**	**KCl**	**NaCl**	**$CaSO_4$**	**Clay**	**KCl**	**NaCl**	**$CaSO_4$**	**Clay**
Magnetics	59.37	0.2	0.4	27.6	71.8	5.1	0.8	82.8	87.7
Washings	1.2	8.9	30.4	12.3	48.5	4.7	1.3	0.8	1.2
Nonmag-netics	39.1	5.4	72.9	8.4	13.9	90.2	97.9	16.5	11.1
Feed	100.0	2.3	28.9	19.9	48.9	100.0	100.0	100.0	100.0

insoluble impurities such as clay and gypsum by causing them to coflocculate with fine particles of magnetite. The magnetic aggregates produced are subsequently separated using high-intensity magnetic separation. The halite and sylvite do not flocculate and remain nonmagnetic. After magnetic removal of the insoluble slimes, the nonmagnetic product is sized following sylvite and halite flotation. Metallurgical balance using magnetite–flocculant method is presented in Table 36.3.

36.5 Other potash ore processing methods

A number of studies were carried out to examine beneficiation of potash ores using alternative methods. These include:

1. Electrostatic separation
2. Heavy media separation

36.5.1 Electrostatic separation method

This method involves preheating of the ore to about 400–500 °C, followed by electrostatic separation. Preheat temperature depends on the amount of the clay in the feed. If the slime associated with the ore is present, then preheating temperature increases. In these studies, the optimum preheat temperature [9] is between 200 and 350 °C.

This method has been tested in the pilot plant scale but has never been introduced to the plant scale.

36.5.2 Heavy liquid separation

Heavy liquid separation although extensively examined, has limited commercial application. Heavy media density used in the studies is in the range of 2.02–2.12. One heavy liquid used is acetylene tetrabromide diluted to the above density with a miscible solvent. Another suitable media can be made from finely ground magnetite, which is added to brine saturated with potassium and sodium chloride.

If clay is present in the ore, it must be removed by using magnetite as a heavy media. High grade of 50% K_2O is difficult to achieve by this technique, particularly in the coarse-size range.

36.6 Commercial operation

There are a fairly large number of operations around the world, especially in North America, which produce potash mainly from solids deposits.

Virtually all plants use the flotation method on sized feed. In the presence of insoluble slimes, the slime is removed using one of the methods described in this chapter. The actual flow sheet varies from plant to plant and the flow sheet configuration depends on the ore.

Some of the plants use the flow sheet shown in Figure 36.6. This flow sheet is practiced when the ore contains small quantities of insoluble slimes.

Clay minerals present in the ore are removed before flotation. Simplified flow sheet that treats clay-containing ore is shown in Figure 36.7. The variation in this

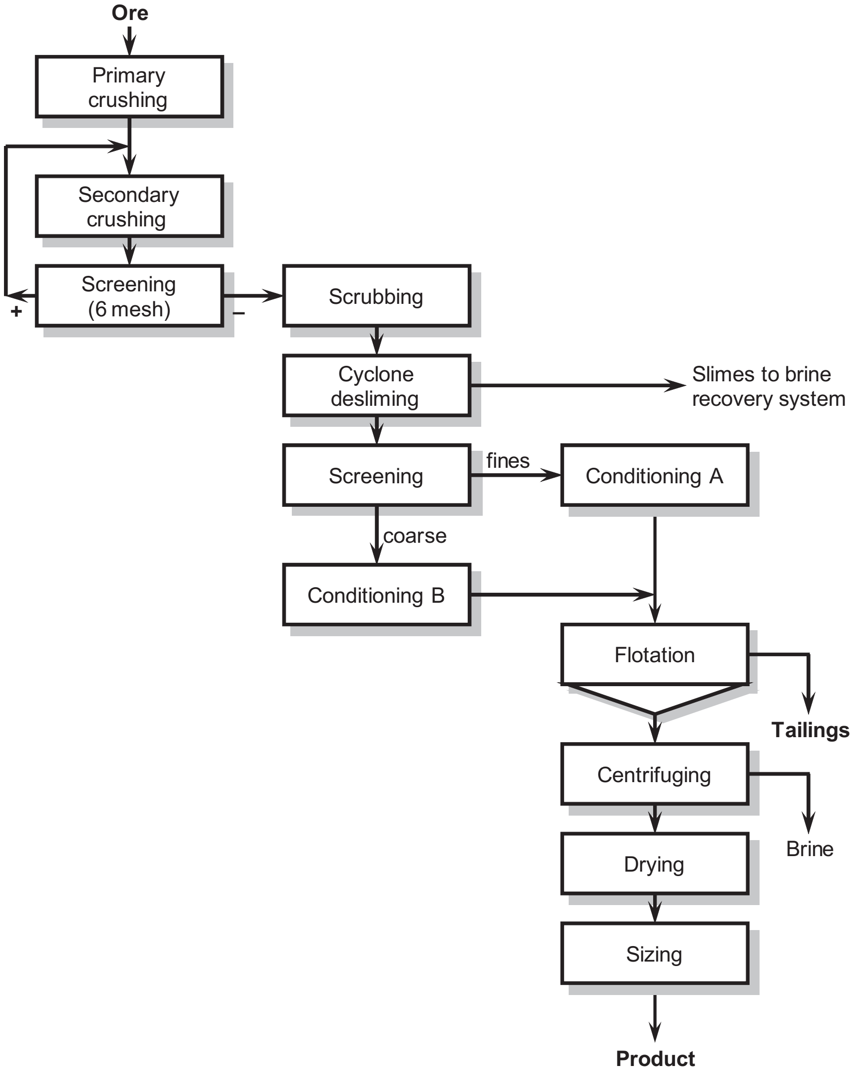

FIGURE 36.6

Simplified flow sheet used in some commercial operations.

flow sheet involves stage grinding and recycling of intermediate products. Clay is recovered in a hydroseparator and further treated to recover brine.

Standard practice in operating plants involves separate treatment of coarse and fine fractions.

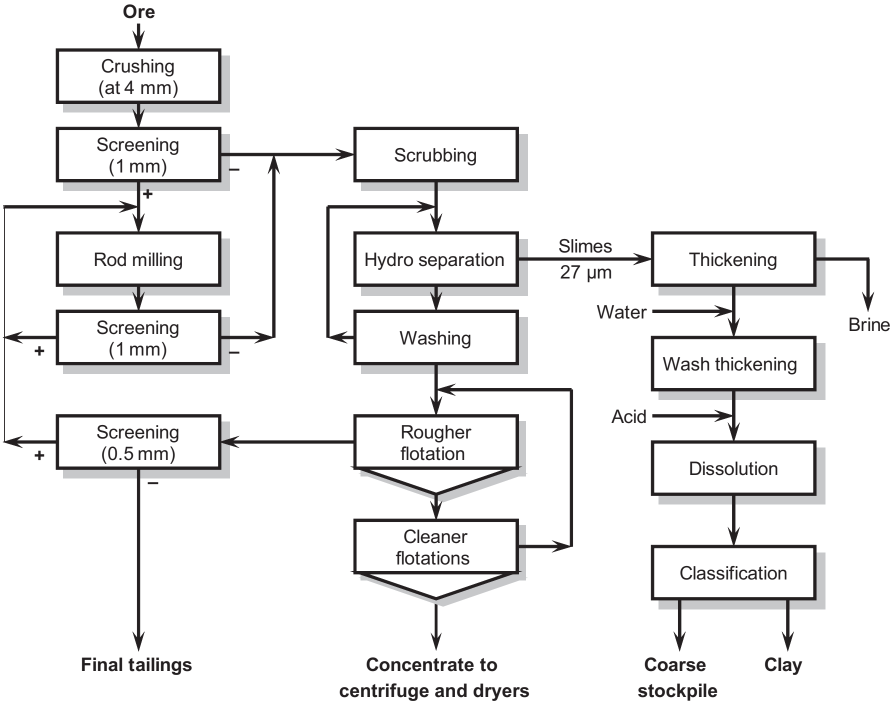

FIGURE 36.7

Simplified flow sheet used for beneficiation of clay-containing ores.

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CHAPTER

Beneficiation of Graphite Ore

37

CHAPTER OUTLINE

37.1 Introduction

The best quality graphite product is coarse-grained (larger than 300 μm) and has 98% carbon or higher. It is considered that graphite mineral is easy to float. However, the treatment flow sheets can be relatively complex and depends on the type of ore to be treated.

The conventional technology for upgrading graphite ore involves milling followed by flotation, regrinding, and multiple cleaning. In spite of that, graphite floats easily with the middling particles adhering to the graphite flakes are reported to the concentrate.

Regrinding of the concentrate also breaks coarse particles of graphite, which represent a problem of producing coarse high-grade graphite.

37.2 Graphite deposits

Graphite deposits have been classified in various ways. Cameron and Weis [1] recognized five groups of deposits on the basis of properties such as grain size (flake or amorphous), host rock type, deposit morphology, and type of metamorphism. Other classification generally divides graphite deposits into three types on the basis of grain size or host rock geometry. Other ore classification [2] includes tripartite division

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into disseminated flake deposits, amorphous graphite deposits, and veinated flake deposits.

Disseminated graphite flake deposits are commonly found regionally metamorphosed siliceous rocks. Flake graphite deposits are usually strata-bound and the graphite is confined to a particular zone within host rock. Flake deposits are found in a number of countries (i.e., Austria, Canada, China).

Disseminated graphite flake deposits are found in carbonaceous sedimentary rocks. The size and shape of these deposits are variable.

Amorphous (microcrystalline) graphite deposits are composed of continental margin or intercratonic-basin metasediments containing coal beds or other highly carbonaceous sedimentary beds. The host rocks are commonly quartzites, phyllites, and conglomerates. The quality of graphite obtained from these deposits is dependent on the characteristics of the original carbonaceous sediments and on the extent of graphitization.

Graphite vein deposits are found in regionally metamorphosed areas, usually in granite and/or charnockite facies rocks. They may be found associated with disseminated graphite flake deposits and are hosted by schist, quartzite, and marble. Granitic intrusive rocks and pegmatites may be associated with the graphite veins. Deposits consisting of graphite quartz, feldspar, calcite, garnet, and sulfides are the veins formed within fractures opened by folding and faulting.

Lamp and chip graphite is primarily produced from these deposits found in India, the USA, and England.

Although the flotation process is relatively simple, the treatment flow sheet is dictated by the type of deposits.

37.3 Beneficiation of graphite ores

37.3.1 Research and development

Little research and development work was performed over the years, due to the fact that liberated graphite is naturally floatable using mainly frother (MIBC, pine oil, and fuel oil). In some cases, coal oil is used in place of fuel oil. It has been reported that coal oil is more selective than fuel oil. Depending on the type of gangue minerals, standard depressants used are sodium silicate, lactic acid, and some of the calcite depressants such as lignin sulfonite. In recent years, extensive research work was conducted by the Indian Bureau of Mines on the development of a new flow sheet and reagent scheme for beneficiation of graphite from the Sivaganga deposit assaying 12.5% FC and 21.64% FC (FC = Fixed Carbon).

In these studies a new collector mixture and flow sheet was developed that is capable of producing a high grade of FC of over 96% C. The new collector IBM/07 is a mixture of different hydrocarbons and terpens [3].

The flow sheet developed in these studies is shown in Figure 37.1. In this flow sheet the rougher concentrate was reground before subsequent cleaner using a special

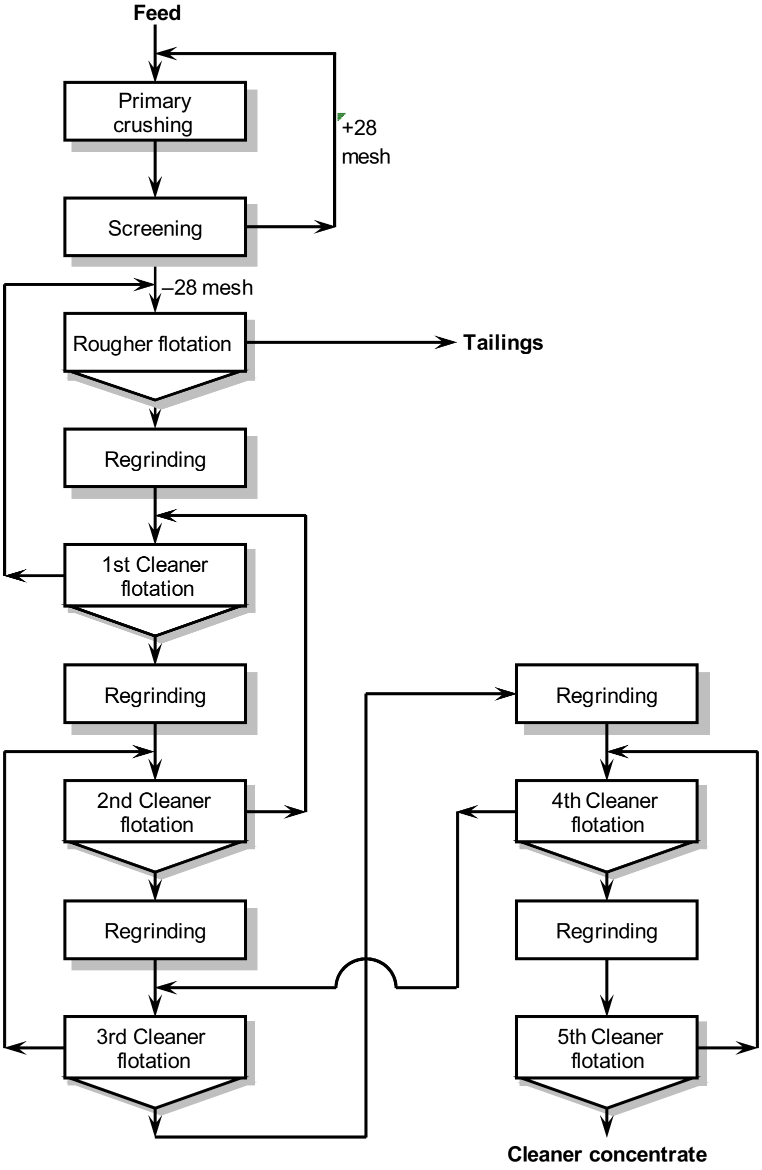

FIGURE 37.1

Flow sheet developed for production of coarse high-grade crystalline graphite.

mill. This regrind is designed to delaminate middling particles without overgrinding of graphite flecks. This is a slow speed regrind mill equipped with flint pebbles.

The effect of new mixture and standard reagents (i.e., fuel oil, pine oil) is shown in Table 37.1.

Table 37.1 Effect of IBM/D7 Mixture and Standard Fuel Oil, Pine Oil on Crystalline Graphite Flotation

	Collector IBM/D7			Fuel Oil, Pine Oil		
Product	**Wt%**	**Assays % FC**	**Distribution % FC**	**Wt%**	**Assays % FC**	**Distribution % FC**
Clean concentration	13.5	96.69	78.0	16.2	90.89	91.0
5th cleaner tail	1.1	81.71	5.4	1.0	26.45	1.6
4th cleaner tail	1.6	65.03	6.2	2.1	13.16	1.7
3rd cleaner tail	2.7	22.59	3.7	5.0	5.59	1.8
2nd cleaner tail	8.8	5.49	2.9	8.7	1.75	0.9
1st cleaner tail	17.6	1.83	1.9	15.5	1.14	1.1
Tougher tail	54.7	0.59	1.9	51.5	0.60	1.9
Head calculated	100.0	16.73	100.0	100.0	16.19	100.0

Using a reagent mixture, high-concentrate grade was achieved at 78% FC recovery. Fuel oil, pine oil produced higher recovery of 91% FC but at lower concentrate grade. The high-grade concentrate obtained using collector mixtures has low impurity levels.

37.3.2 Process for production of coarse flake graphite

Very often particles of waste are attached to the graphite flakes and reports to graphite concentrate resulting in a low-grade concentrate. Ball mill or pebble mill regrind would liberate graphite but would also produce fine graphite. During studies between 1992 and 1993 at MINEC (South Africa) a unique delamination technique was developed that separates graphite flakes and removes attached gangue minerals with little damage to the graphite flakes themselves. This process was tested in Zimbabwe Development Corporation Graphite Mine. Using the new delamination technique, a graphite concentrate grade has been improved from 90% FC to 98% FC [4]. It has been also reported that delamination of graphite middling using a slow-speed ball mill with flint pebble grinding media was successful.

37.3.3 Graphite beneficiation flow sheet

37.3.3.1 Introduction

Although the reagent scheme used for beneficiation of graphite is simple due to the fact that graphite passes natural flotability, most of the operations around the world use frother and hydrocarbon oil (kerosene, fuel oil, phenol). Depressants such as sodium silicate and/or lactic acid are used for beneficiation of ores with complex mineral composition.

One of the main problems during beneficiation of graphite ore is the liberation to avoid production of fine graphite. In a number of cases, gangue particles are attached to graphite flecks and require delamination, to avoid breaking of larger flecks. The highest demand for graphite is coarse high-grade concentrate.

37.3.3.2 The flow sheets

The operating plant flow sheets depend on the type of ore to be treated and liberation characteristics of the graphite. The flow sheet can be relatively complex to simple. Several examples of the flow sheet are presented below.

A flow sheet for the production of flake graphite is presented in Figure 37.2. This flow sheet utilizes concentrate regrind in the rod mill in the initial cleaning stages (clean 1–3). In the last cleaning, attrition mills were used. Using this flow sheet, two grades of flake graphite were produced: a concentrate assaying 95% C and a premium concentrate assaying 99% C after chemical treatment.

The Nanshu Graphite Mine is another example of a graphite complex flow sheet. The flow sheet is presented in Figure 37.3.

Using this flow sheet, several concentrates were produced at different sizes, ranging from 90% C to 95% C. The overall recovery of graphite combined concentrates is 88% C.

An example of a simple flow sheet is the flow sheet used at Bogala Mine in Sri Lanka. The flow sheet is shown in Figure 37.4.

The concentrator treats high-grade ore assaying 87–88% C. The flow sheet uses open circuit grind followed by rougher flotation and a single cleaning stage. The cleaner concentrate was treated on the table where three different grade concentrates were produced, ranging from 90% C to 95–97% C, and higher than 97% C. Each concentrate is a flake type concentrate.

A similar flow sheet has been developed at Merelani operations—Tanzania, where large flake graphite concentrate was produced at a grade ranging from 96% C to 99% C after delamination. Delamination was performed in a low-speed ball mill at low pulp density 30–40% solids.

37.3.4 Graphite producers and its application

There are more than 100 operating plants in China, Australia, South and North America, Europe, Africa, and the Soviet Union. Each of these operating plants produces different types and quality of graphite that are used in different applications.

In general, the flow sheet varies from plant to plant while the reagent does not vary significantly.

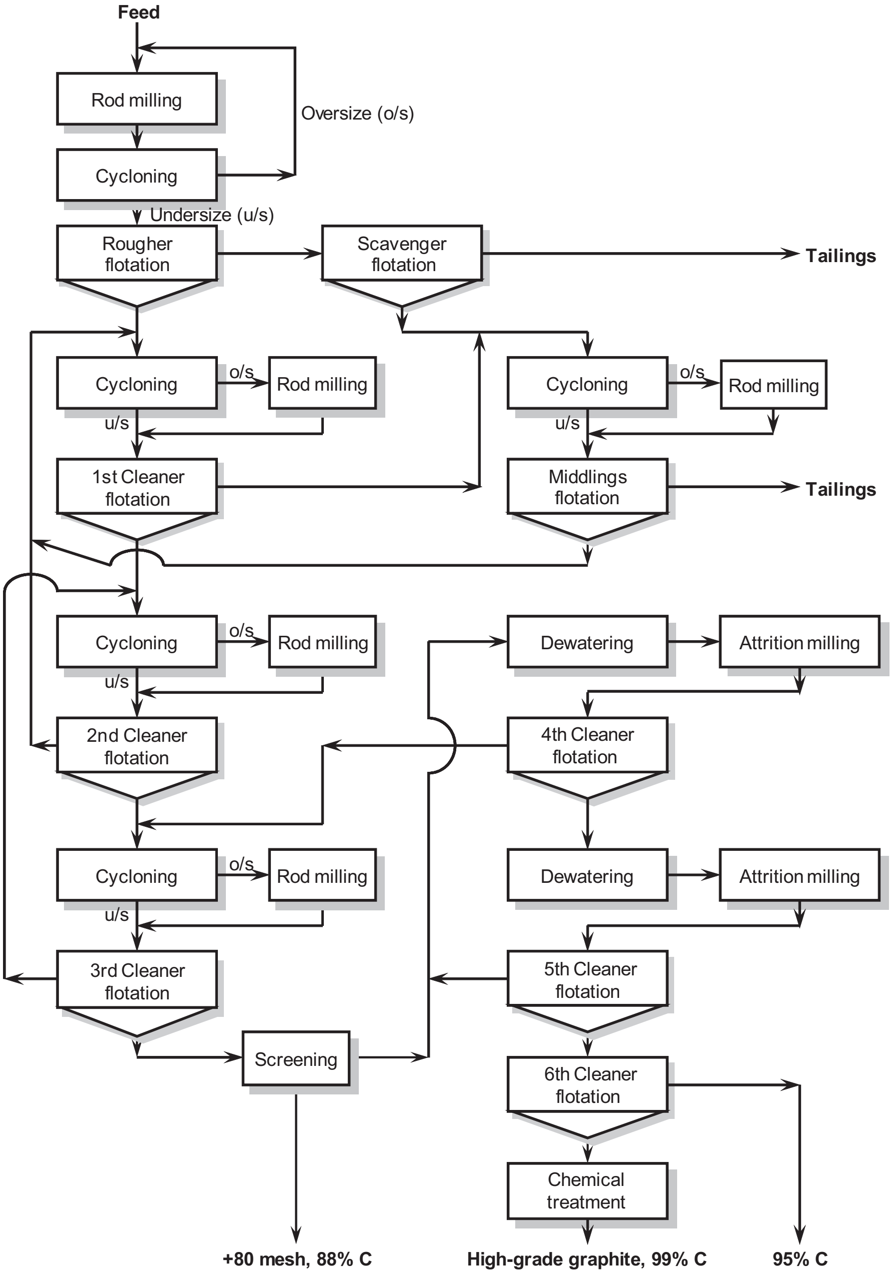

FIGURE 37.2

Concentrator flow sheet recommended for production of flake graphite.

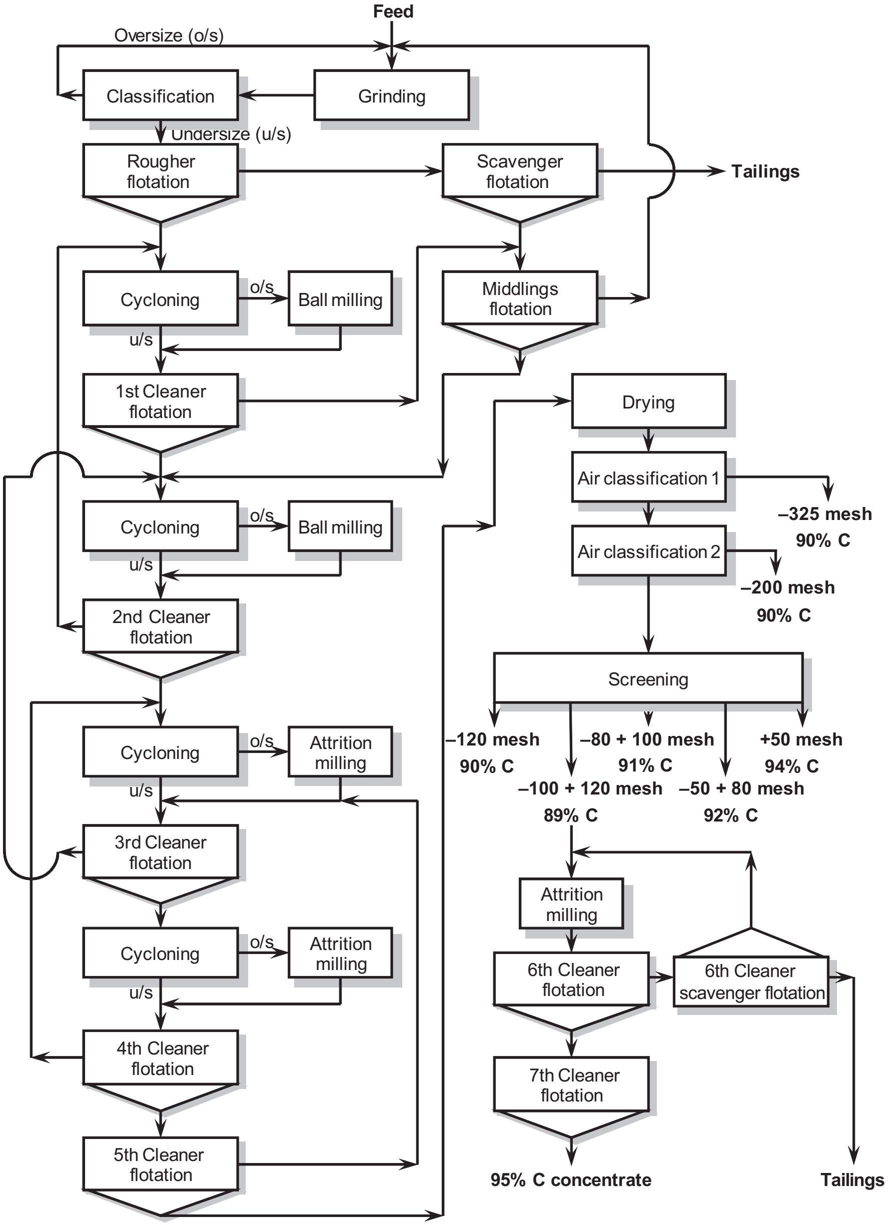

FIGURE 37.3

Concentrator flow sheet of Nanshu graphite mine.

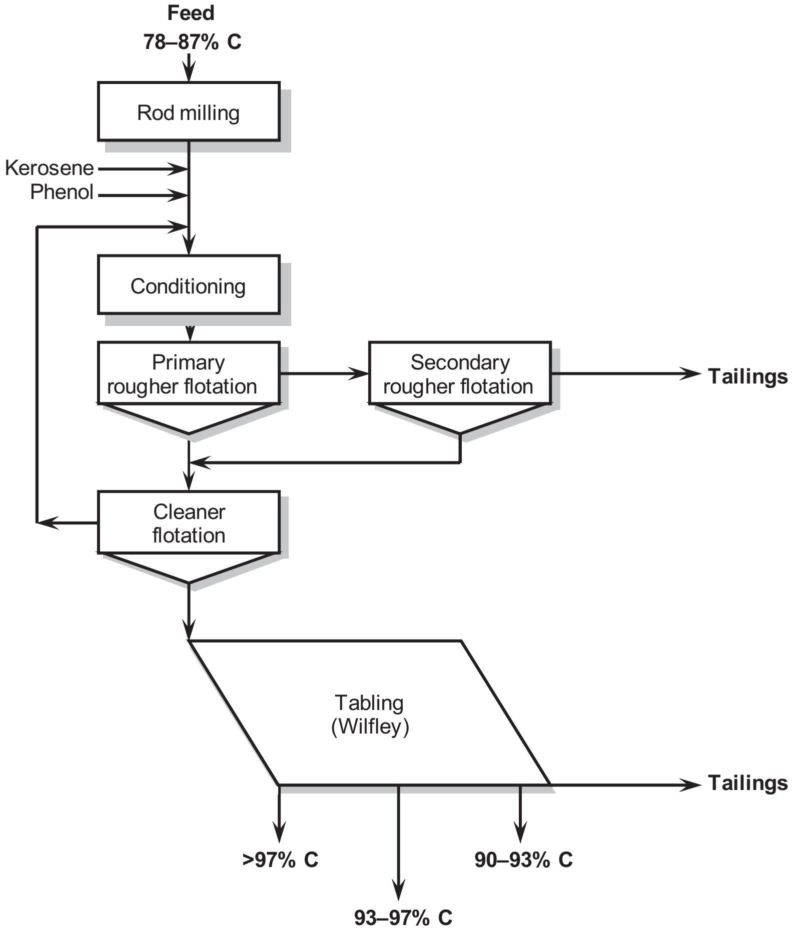

FIGURE 37.4

Flow sheet used in Bagola mine—Sri Lanka.

It should be noted that some operating mines in Norway have introduced polypropylene glycol butyl ether as a frother, which is claimed to improve selectivity and graphite recovery significantly (Table 37.2).

Table 37.2 Summary of Graphite Quality and Its Application—From various Producers

Crystalline Flake	Natural Microcrystalline, Amorphous	Crystalline Vein/Lamp	Treated Exfoliated Expended	Treated Colloidal
Application				
Batteries Carbon pans Carbon brushes Catalysts Coatings Foils Friction material Fuel cells Lubricants Pencils Plastics and resins	Carbon additives Coating Friction, materials Lubricants Pencils Refractories – – – – –	Batteries Lubricants	Batteries Coverings Foil Flame retard Gaskets Insulation Lubricants Paint Seals	Batteries Carbon, resistance filler Catalysts Conductive suspension Lubricants Metal alloys Mold release agent
Producers				
China India Brazil Canada Mexico Norway Zimbabwe Madagascar	Austria China Czech Republic Northern Korea Mexico	Sri Lanka	India Switzerland	India Ukraine

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CHAPTER

Beneficiation of Mica-Containing Ore

38

CHAPTER OUTLINE

38.1 Introduction

There are several types of mica minerals present in the various types of ore bodies that contain lithium, base metal ore, and other oxide ores. In a number of cases mica has to be removed before flotation of either lithium or other oxide minerals.

In the literature it has been quoted that flotation properties of various mica minerals are similar. However, many of the references found in the literature did not make mention of mineral types that were used in the studies.

Mica can be floated using anionic or cationic collectors or a combination of the two in the presence of gangue depressants, which can be aluminum sulfate, sodium silicate, and other organic depressants.

The lead nitrate and alkaline earth salts act as an activator for mica. Iron and aluminum salts have a depressing effect on mica minerals. Apart from mica types of deposits, mica can be part of the base metal deposits as well as Rare earth oxides [REO] deposits. Mica has to be removed from the ore before other minerals can be floated.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00038-5

38.2 Mica minerals and deposits

The mica forms a series of complex silicates of aluminum with potassium and hydrogen, magnesium with ferrous iron, and in some varieties, sodium lithium ferric iron with main gangue minerals. More rarely manganese, chromium, fluorine, and titanium are usually present in small amounts.

The important mica minerals are as follows:

1. Muscovite: $KAl_2[AlSi_3O_{10}](OH,F)_2$
2. Lepidolite: $K_2(LiAl)_6[SiAl_2O_{20}](OH,F)_4$
3. Biotite: $(HK)_2(MgFe)_2Al_2(SiO_4)_3$
4. Phlogopite: $H_2Mga_3Al(SiO_4)_3$
5. Lepidomelane: $(HK)_2Fe_3(FeAl)_4(SiO_4)_5$

Lepidolite, with muscovite and phlogopite are the most important commercial minerals for the production of mica.

Mica is contained in pegmatite ore bodies that, in most cases, contain either lithium or rare earth oxides. Biotite is a major mica mineral present in a number of major polymetallic deposits of igneous origin, and is rich in iron and magnesium.

38.3 Research and development on flotation of mica minerals

Extensive research work was carried out by a number of researchers [1–4]. In these works, a process for separation of mica from other silicate minerals using either anionic or cationic collectors was studied. When using cationic collectors, either lead nitrate or alkaline earth salts are used as a mica collector.

Cationic flotation of mica was carried out using short-chain amine in the acid circuit in conjunction with aluminum sulfate as a silica mineral depressant.

In some studies a tallow amine acetate collector was used [4] to float mica from beryl-containing pegmatites. Tests were performed at pH 2.5. This collector was also recommended to remove mica from mixed spodumene mica concentrates.

In this study [5], a reagent scheme was described consisting of oleic acid and coco amine acetate. The flotation was conducted in alkaline pH using soda ash as a pH modifier. Metallurgical results obtained using 150 g/t oleic acid and 40 g/t coco amine acetate are shown in Table 38.1.

The concentrate produced assayed about 98.3% mica with 81.3% mica recovery.

When using distilled tall oil in place of oleic acid with coco amine acetate, similar metallurgical results were obtained as obtained with oleic acid (Table 38.2).

In this study, mica from Carolina, the USA was used.

It is confirmed that using fatty acid and coco amine acetate collector system gave good metallurgical results in alkaline pH.

A selective flotation of muscovite-containing quartz and feldspar was studied using a collector system consisting of sodium oleate and dodecylamine acetate [5].

Table 38.1 Mica Flotation Results Obtained Using Oleic Acid–Amine Collector System

Product	Wt%	Mica Assays %	Mica Recovery %
Mica combined concentration	14.2	98.3	81.3
Mica middlings	4.0	6.8	1.9
Mica tailing	73.6	3.7	15.9
Slimes	8.2	2.1	0.9
Head (calculated)	100.0	17.9	100.0

Table 38.2 Mica Flotation Results Obtained Using Tall Oil Fatty Acid and Coco Amine Acetate Collector System

Product	Wt%	Mica Assays %	Mica Recovery %
Mica combined concentration	23.00	97.4	84.5
Mica middlings	11.40	23.7	10.2
Mica tailing	54.30	1.0	3.9
Slimes	11.3	3.3	1.4
Head (calculated)	100.0	26.5	100.0

Muscovite was found to float in preference to biotite when the pulp was stage conditioned first with sodium oleate followed by amine in an alkaline pH. About 63% of muscovite at 93% recovery was achieved in this study.

38.4 Flotation of individual mica minerals biotite $(HK)_2(MgFe)_2Al_2(SiO_4)_3$

In the literature it has been established that flotation of biotite depends on the degree of alteration. The flotation of biotite has two maxima. It floats at highly acidic conditions (i.e., pH 1) or under mildly alkaline pH when using dodecylamine (C14).

It has been found that sodium fluoride and calcium salts activate biotite when using amine collectors. In the other studies [6], it has been shown that maximum biotite recovery was achieved at pH 4, which is in contradiction with previous studies.

It has been suggested that the flotation of biotite is dependent upon weathering that has occurred, so when using cationic collectors the highly weathered material floats at pH 1and the unweathered part at pH 7 [7].

Fluorosilicate and/or pyrogallol has a depressing effect on biotite when using anionic collectors. The actual flotation parameter data using acid or alkaline conditions are shown in Table 38.3.

Table 38.3 Muscovite Flotation Reagent Scheme

Flotation Method	pH	Reagent Type	Addition Rate g/t
Acid	2.4	H_2SO_4	100–1500
		Armac T	200–250
		Pine oil	20–30
Alkaline	9.8	NaOH	To pH
		Na_2CO_3	500–1000
		Na_2SiO_3	300–500
		Armac T	100–120
		Oleic acid	300–500

Table 38.4 Effect of Fineness of Grind on Lepidolite Flotation

Grinding Size, μm	Concentration Wt%	Concentration Grade % Li_2O	Recovery %
290	45.5	2.37	68.3
208	52.6	2.8	78.5
147	56.7	2.8	83.9

This reagent scheme applies to unweathered muscovite.

38.4.1 Lepidolite $K_2(Li,Al)_6[Si_6Al_2O_{20}](OH,F)_4$

Lepidolite has good flotation properties using dodecylamine in a pH range from 2 to 11. Flotation characteristics of lepidolite are somewhat different from those of biotite. Flotation research was carried out using ore that contains silica and feldspar [8]. Using dodecylamine acetate at a natural pH, a concentrate grade of 2.5% lithia at 67% recovery was achieved. In the testwork in which different amines were examined, it was found that hexadecylamine acetate (Armac 16D) gave the best metallurgical results. The maximum grade and recovery were achieved at pH 3.5. The metallurgical results were also related to fineness of grind and pulp density. Flotation of lepidolite was improved at a lower pulp density. The effect of fineness of grind on lepidolite grade and recovery is illustrated in Table 38.4.

Research work was performed on the ore containing lepidolite, spodumene, petolite, and feldspar [9]. It has been demonstrated that using tallow amine acetate at pH 2.5 concentrated by HCl over 85%, lepidolite was recovered in a concentrate assaying 2.2% Li_2O.

38.4.2 Muscovite $KAl_2[AlSi_3O_{10}](OH,F)_2$

The flotation properties of muscovite are very similar to lepidolite. Flotation of muscovite starts at pH 2–11.5.

Extensive development testwork on muscovite flotation was carried out by US Bureau of Mines [10]. For example, in an ore containing 16.5% muscovite, 77% quartz, and 4.5% kaolin, the muscovite was floated at pH 4.0–4.5 using sulfuric acid and collector coco amine acetate plus kerosene. Under these conditions, a concentrate grade assaying 98% muscovite at 95% recovery was achieved. Other collectors examined include a mixture of stearyl and oleyl amine. Using this collector, a high-grade concentrate was achieved at about 70% recovery.

A second muscovite flotation method examined involves a combination of anionic and cationic collectors [11]. Using this method oleic acid or a mixture of oleic and linoleic acid and tallow amine acetate was used. The flow sheet developed using this method is shown in Figure 38.1. Muscovite was floated at pH 9.7. Using these conditions (Figure 38.1), a concentrate assayed 96.5% muscovite at 70% recovery was achieved. The results obtained were better than those achieved with amine at acid pH.

Replacing sodium silicate with lignin sulfonate at pH 9.2 resulted in the improvement in muscovite recovery.

In studies [12], it has been shown that with no modifiers present, muscovite floats most readily under alkaline conditions with cationic collectors, diamines giving the best metallurgical results. However, the recoveries obtained with primary amines were considerably improved by additions of activators such as fluoride, iron salts, and citric acid.

38.4.3 Other mica minerals

The flotation properties of phlogopite, lepidomelane, and others have not been extensively studied and no particular references on their flotation exist.

38.5 Commercial beneficiation plants

38.5.1 Introduction

There are a considerable number of mica producers around the world from Australia, Asia, Africa, Europe, and America.

Ore mined from flake mica deposits requires considerable processing to separate mica and any by-products from the gangue minerals. The number of operations varies according to the nature of the deposit and the extent to which the products are recovered.

Three general methods are used to concentrate and recover mica as the primary product from the run of mine ores.

The simplest process that separates mica from the gangue material is differential crushing and screening in washer plants.

Another method concentrates the differentially ground ore by using screens, classifiers, and spirals. The third method concentrates the ore screen classifiers and flotation.

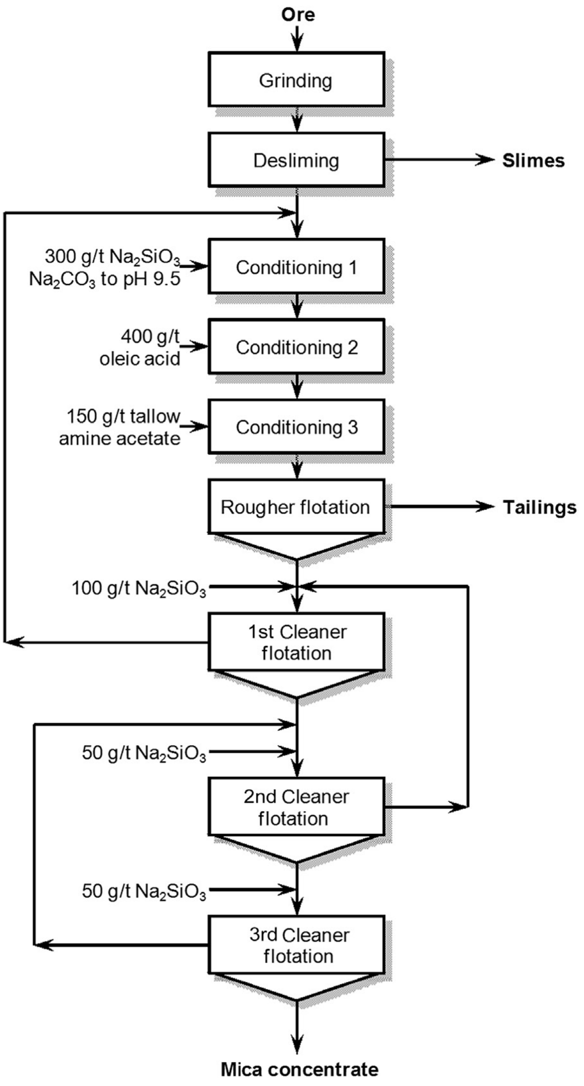

FIGURE 38.1

Flow sheet with point of reagent addition used in anionic–cationic flotation method.

38.5.2 Plant flow sheets using combination of grinding and gravity

Grinding of mica ore is one of the most difficult parts of commercial plants. Some of the properties, which make mica useful, make it difficult to grind. Even tin flakes are tough and elastic and resist abrasion and reduction in size by the conventional types of grinding equipment.

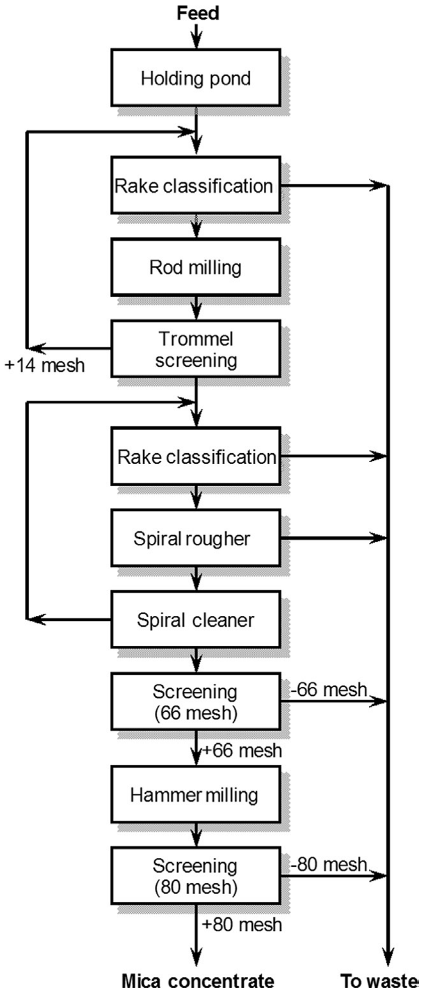

FIGURE 38.2

Flow sheet using grinding and gravity for recovery of mica.

Two processes, dry grinding and wet grinding are used in operating plants to produce ground mica. The products of the two grinding methods differ from each other in certain physical properties. Most of the plants for beneficiation of mica have dry grinding equipment as a part operating plant.

The flow sheet used in operating plants that use a combination of grinding and gravity is shown in Figure 38.2.

38.5.3 Commercial plants flow sheets that used flotation

The use of flotation permits the recovery of finer size mica than can be produced by the gravity method. Therefore, the overall recovery of mica is much higher than that obtained using gravity.

Flotation plants usually utilize acid cationic method, alkaline anionic method, and combination of the two methods.

Commercial flow sheet configuration depends on the flotation method used as well as on the type of ore treated.

The example of the operating plant flow sheet that uses cationic flotation method is shown in Figure 38.3.

This flow sheet is relatively complex and involves several stages of fines before removal. Mica is also floated in two stages.

The flow sheet that uses alkaline anionic–cationic flotation method treats ore containing feldspar as a major gangue mineral, in which case, acid cationic flotation cannot be used since feldspar also floats in the acid circuit with similar collectors.

The flow sheet involves attrition scrubbing followed by desliming and mica flotation. Mica tailing is deslimed followed by mica iron flotation. The tailing is deslimed followed by feldspar flotation. Feldspar is floated in an acid circuit using cationic collectors after activation. The plant flow sheet using alkaline anionic–cationic flotation method is presented in Figure 38.4.

In some cases the valuable mineral in the ore is feldspar, in which cases mica becomes a by-product.

The plant flow sheet that uses a combination of acid cationic and alkaline anionic–cationic flotation method is used during the treatment of weathered micaceous pegmatite ore. The flow sheet involves split circuit mica flotation, where in stage one, coarse mica is recovered using the cationic acid flotation method. In the second stage, fine mica was recovered using the alkaline anionic–cationic method. The plant flow sheets using combination of acid and alkaline flotation method is shown in Figure 38.5. These flow sheets are relatively complex and are practiced in a number of operations in India and China.

38.6 Commercial mica

Commercial mica has different sizes and qualities depending on the application. Typical chemical composition of commercial mica is presented in Table 38.5.

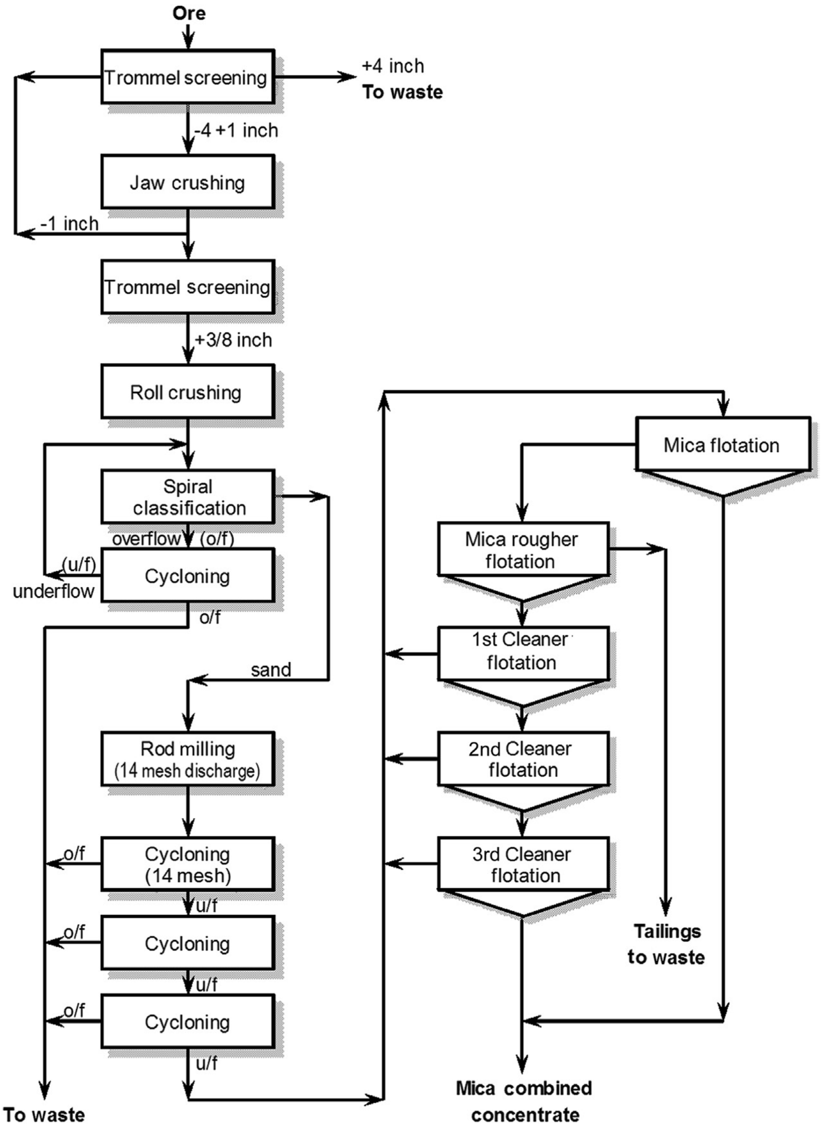

FIGURE 38.3

Plant flow sheet acid cationic flotation method.

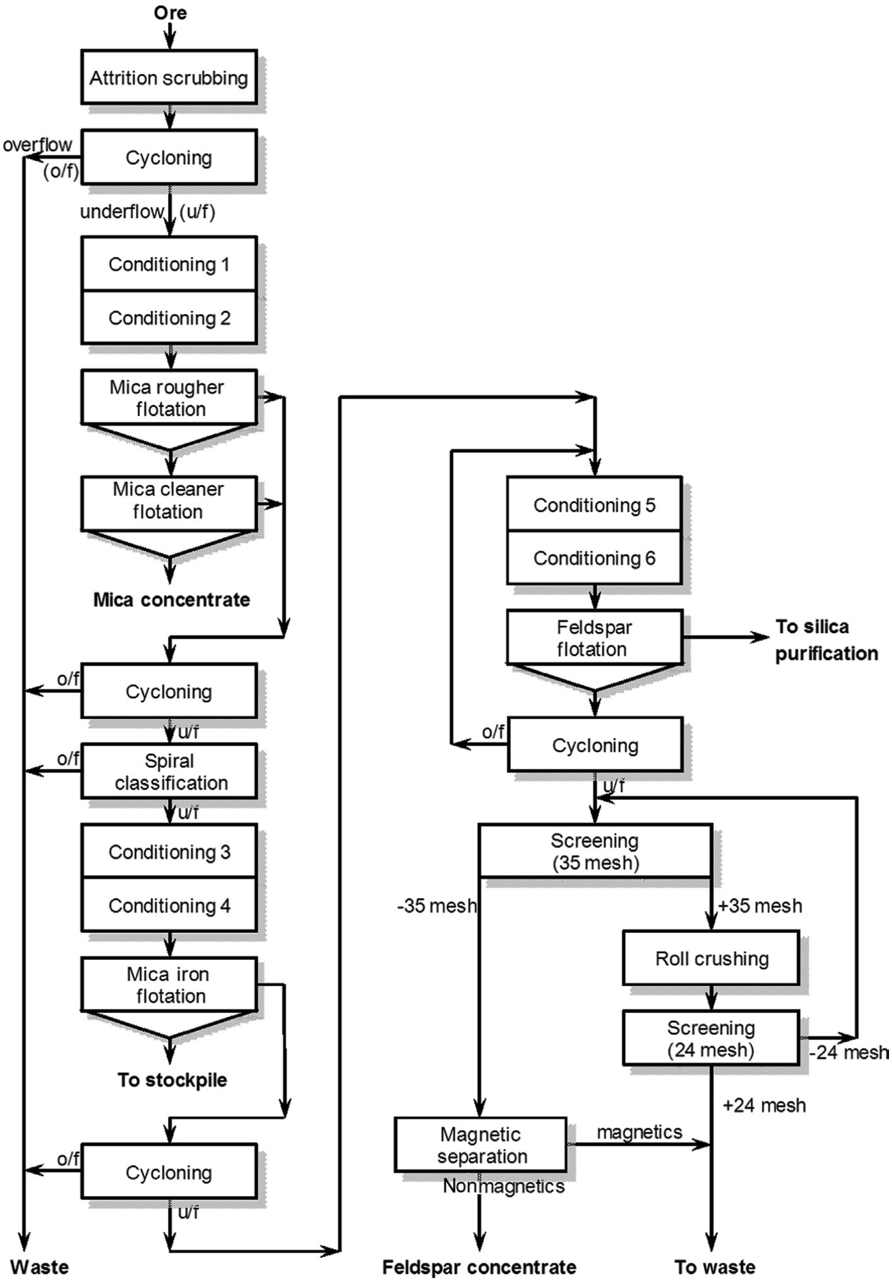

FIGURE 38.4

Concentrators plant flow sheet using alkaline anionic–cationic flotation method.

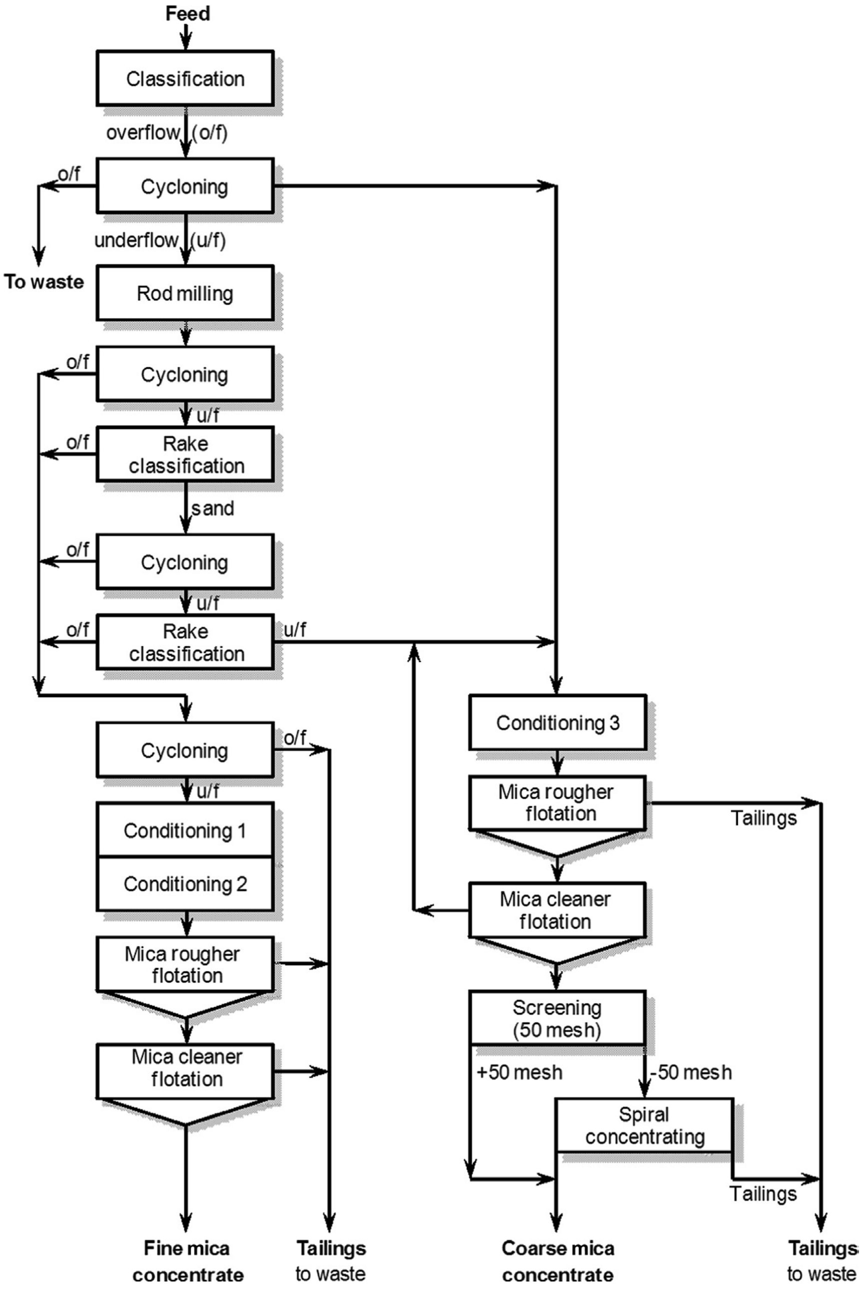

FIGURE 38.5

Plant flow sheets using a combination of acid cationic and alkaline anionic–cationic flotation.

Table 38.5 Chemical Composition of Commercial Mica

	Assays %	
Element	**Muscovite**	**Phlogopite**
SiO_2	44–47	37–43
Al_2O_3	30–38	12–17
Fe_2O_3	0.2–5	0.2–2.0
K_2O	8.5–11.5	8.5–11.5
Na_2O	0.1–0.8	0.3–0.8
TiO_2	0.0–0.9	0.0–1.5
BaO	–	0.0–0.7
MgO	0.3–1.5	23–29
CaO	0.1	0.1–0.5
Li_2O	0.1–0.8	0.0–0.1
F	0.0–0.15	0.5–5.0
P	Trace	Trace
S	Trace	Trace
LOI	4–5	1–3

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CHAPTER

Beneficiation of Coal

39

CHAPTER OUTLINE

39.1 Introduction

Coal is considered one of the most important sources of energy in the world.

In the early days of the industry, coal was mined and delivered without any treatment to its point of consumption. Coal as mined is considered a raw material, which required treatment to remove impurities such as pyrite and ash.

Over the past several decades, a number of coal upgrades have been developed to remove impurities such as ash and pyrite. Some of these methods include: washing, gravity concentration, agglomeration flotation.

A large portion of the effort has been placed on sulfur reduction. The major problem in sulfur reduction represents the presence of organic sulfur, which is impossible to remove. Selection of the coal treatment method largely depends on the coal formation (genesis) and the particle size. For example, fine coal can only be beneficiated using the flotation method.

39.2 Coal genesis

Coal is a combustible mineral substance resulting from the degradation and alteration of vegetable matter largely in the absence of air. Coal deposits in North America can be of the Permian age or cretaceous and tertiary in age. The differences in genesis [1] can result in rather different properties of coal seemingly of the same rank.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00039-7

Table 39.1 Approximate Value of Some Coal Properties in Different Rank Ranges

ASTM Rank	Lignite	Subbituminous	High-Volatile Bituminous	Medium-Volatile Bituminous	Low-Volatile Bituminous	Anthracite
Equilibrium moisture %	35	16–29	12	3	3	5.5
Volatile matter %	33–62	60	34–52	20–31	10–20	<10
Calorific value BTU/LC	7000	10,000	12,000	15,000	15,800	15,200
Calorific value kJ/kg	16,000	23,000	28,000	35,000	37,000	35,000
Average %C	73	76	80	89	91	95.35
Range %C	66–76	71–81	76–84	86–92	87–92	92–97
H%	4.5	5	5.5	4.5	3.5	2.5
O%	25–16	25–11	18–8	4–3	3	2
O as OH%	11–7	9–5	9–4	3–1	3–1	1–0
O as COOH%	10–6	9–4	Low	0	0	0
Aromatic C atoms of total	50	65	–	80–85	85–90	90–95
No. of benzene ring layer	1–2	–	2–3	2–3	18	4
Friability avgerage %	12	20–30	43	70	70	33

The chemical and physical properties of different coal origins are shown in Table 39.1.

From Table 39.1 a regular progression in the various chemical and physical properties of coal is seen to proceed from the rank classification. Thus, any one of several rank parameters [2] will provide a general guide to many properties of a particular coal. These properties are useful for the selection of the treatment method.

It is very important to understand coal flotation behavior. Coal flotation is a complicated process and is subject to rational interpretation. To develop an efficient coal treatment process, it is important to know (1) the coal rank and its chemical and physical properties, (2) the general geologic genesis, (3) oxidation pyrite and ash distribution and properties, and (4) the flotation process for different properties of coal.

39.3 Beneficiation of coal

There are a number of methods by which coal is beneficiated and this largely depends on (1) the type of coal, (2) the type of impurities (pyrite, clay ash), and (3) the size of coal particles. The commonly used beneficiation method includes:

- Coal washing
- Gravity separation as a specific spirals
- Heavy media separation
- Oil agglomeration
- Flotation

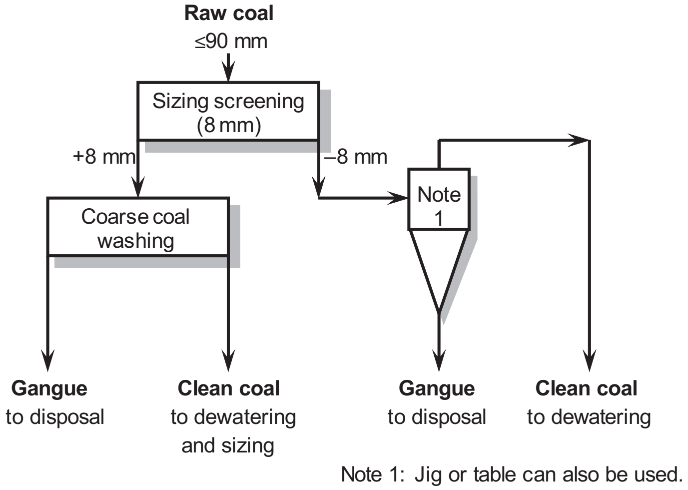
39.3.1 Coal washing

A large number of operating plants use coal washing to remove impurities such as clay ash and pyrite. There are several devices used in coal washing, which include specific jigs, water cyclone, screens, and tables. The washing rejects range from 20 to 38% of the feed.

The flow sheet used for coal washing is presented in Figure 39.1.

39.3.2 Coal gravity separation as a spirals

The use of spirals has become a standard practice in coal preparation plants worldwide. To their credit, spirals typically show very low coal losses [3] in a tailing stream under most operating conditions. However, spirals do tend to separate at cut point in excess of 1.8 S.G. An attempted lower cut point may have typically resulted in coal losses to middlings. To avoid such losses, middling retreatment is performed in secondary spirals. Other forms of retreatment like, cyclone with water washing or heavy media cyclone can be used. In a plant test, combining the two stages, spiral and heavy media cyclone, significantly improved the organic efficiency but ash content



Note 1: Jig or table can also be used.

FIGURE 39.1

Flow sheet used in coal washing.

Table 39.2 Results of Combination of Spirals and Heavy Media Cyclone Obtained on Raw Coal Feed

Clean Coal Stream	Primary and Secondary Clean Coal HMC No. 1 Product	Primary and Secondary Clean Coal and HMC No. 2 Product
Yield	70.24	71.17
Clean coal ash	10.77	12.49
Cut point	1.715	1.797
Organic efficiency	98.9	95.7
Refuse ash	71.38	69.09
Interim yield	17.94	18.87
Increment ash	7.73	14.36

HMC, Heavy Media Cyclone.

was somewhat increased. Table 39.2 shows the results of heavy media cyclone and spirals on raw coal feed.

The flow sheet for combined two-stage spiral and heavy media cyclone circuit is presented in Figure 39.2.

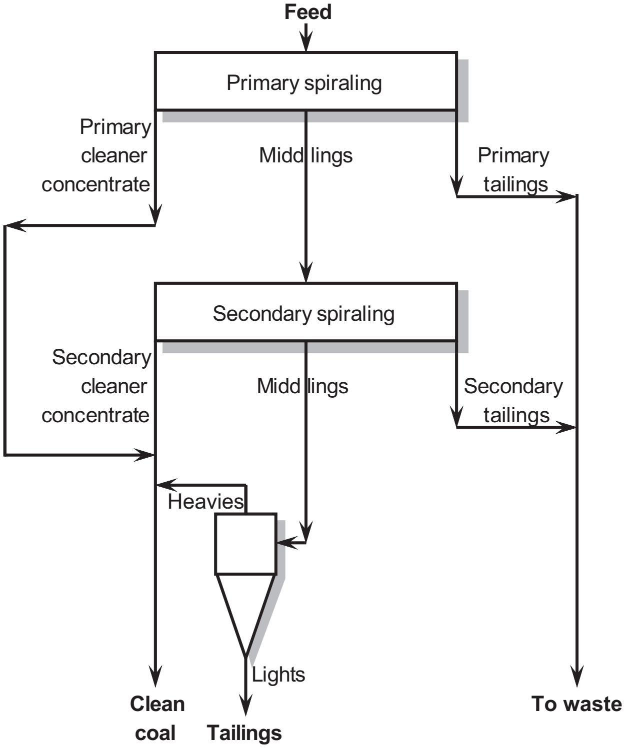


FIGURE 39.2

Flow sheet for combined two-stage spiral and heavy media cyclone circuit.

Table 39.3 Results Obtained on 4 mesh Bituminous Coal Using a Combination of Spiral and Sizer

Product	Assays % Ash	% Weight Distribution
Feed	11.09	–
Coal	6.56	69.1
Middlings	14.74	5.7
Heavy	50.56	5.7

Another concentration method involving combination of spiral and sizer is used in the plants to treat bituminous coal. The feed to the spiral is about –4 mesh nominal size.

Metallurgical results obtained are presented in Table 39.3.

The actual flow sheet employed in the plant is shown in Figure 39.3.

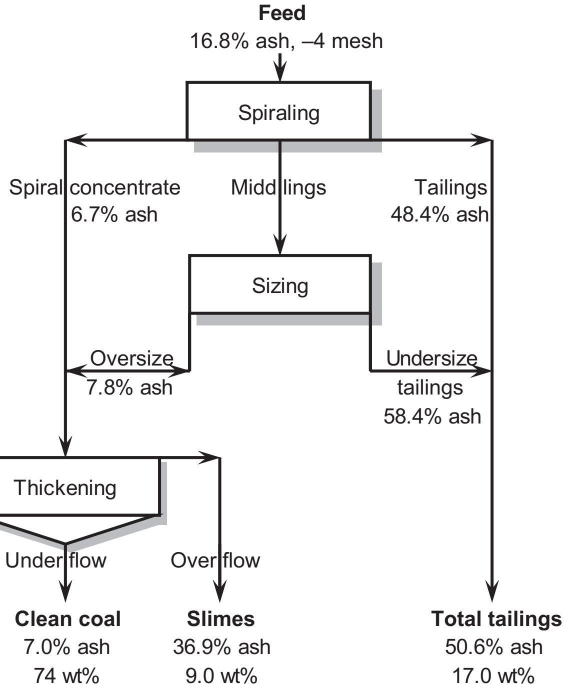


FIGURE 39.3

Flow sheet used for cleaning of bituminous coal using spiral and sizer.

39.3.3 Heavy media separation

Heavy media separation dates back to several centuries. Initially, a fine magnetite was used as a heavy media. In 1936, a plant was designed employing organic liquid as a heavy media for treating anthracite coal containing ore.

The heavy media process is usually used for treatment of coarse coal above 9.5 mm in size. Finer coal below 9.5 mm cannot be cleaned economically in heavy medium. The settling velocities of the fine material are very low, and consequently the time required to separate the lighter coal from the heavy becomes excessive.

Nowadays, magnetic field has been used as a heavy media at fineness of between 100 and 325 mesh. Separation using heavy media can be done in either conventional heavy media, thanks or in heavy media cyclones.

39.3.4 Oil agglomeration

Agglomeration is a process in which a liquid immersible in water is used to “bridge” hydrophobic (oleophilic) coal particle while leaving gangue particles (pyrite, ash, etc.) dispersed in the aqua medium.

High-sheer agitation is needed to displace the water on the surface of the coal with the agglomerating liquid. Agglomerating liquid is typically a heavy oil like diesel fuel or No. 6 fuel oil or a light hydrocarbon like heptane or pentane.

During the high-shear agitation step the organic matter is separated from the pyritic sulfur and other mineral matter components, hence it is often referred to as the cleaning step.

Agglomeration and flotation are the only processes that presently deal with recovery of fine coal. Oil agglomeration has two entirely separable functions. First is its ability to selectively separate coal from mineral matter to produce high-grade coal. Second is the elimination of conventional dewatering of coal.

There are several recent operating plants that use different approaches during oil agglomeration. These differences are smaller than similarities.

Spherical agglomeration process was developed in the early 1960s. Like other processes, spherical agglomeration depends on the preferential wetting of coal particles by a hydrocarbon. The most significant advance of the spherical agglomeration is the degree of compaction. When coal agglomerates are compacted the dewatering is simplified. Figure 39.4 shows the flow sheet used in spherical agglomeration.

Shell pelletizing separator consists of special mixing device for contact oil shoot suspension that resulted in the formation of 305 mm pellets from the diluted suspension. Using this process, a coal recovery of 95% is achieved with 85–95% ash rejection using 9–15% heavy oil in coal slurry.

Olifloc process is aimed at optimizing mineral matter removal and maximizing selectivity. It also maximizes the recovery of coal. The olifloc process is also designed for fine coal product. The flow sheet used in the olifloc process is shown in Figure 39.5.

SFRI process is being used in India for the beneficiation of difficult-to-wash and noncoking coal. The technique conditions fine coal slurry (smaller than 100 µm) with diesel oil (2% by weight of coal) in the colloid mill for 2 min. The conditioned slurry is subsequently agitated with an 8–12% addition of heavy oil followed by washing and screening.

39.3.5 Coal flotation

Coal flotation is practiced in many operating plants around the world. Flotation is applied to fine coal, i.e., 600 µm (30 mesh). In conventional practice the frother and collector are stirred in a water solution before being introduced to the slurry. It should be noted that an excess of reagents is invariably deleterious to the flotation process in terms of the selectivity between the coal and the gangue minerals. However, to achieve high coal recovery an excess of frother and collector will be required which in turn, results in reduced selectivity. Furthermore, an excess of gangue depressants will likely depress the coal.

39.3.5.1 Reagents used in coal flotation

Frothers: The most commonly used coal frothers have been the short, branched-chain alcohols and the creosotes, pine oil, and polypropylene glycol ethers.

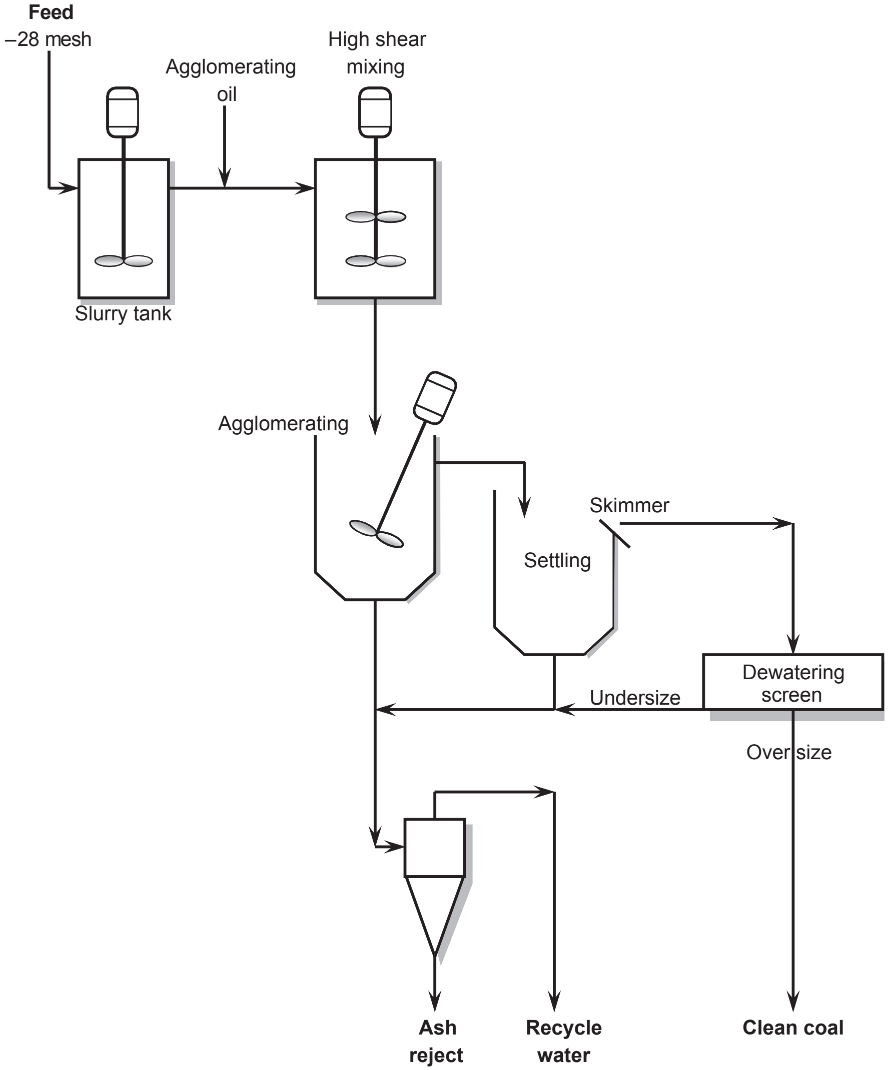


FIGURE 39.4

Spherical agglomeration flow sheet.

The short chain branched alcohols (MIBC) are usually considered to be a main frother in the flotation of the higher rank coals but an excess has been demonstrated to promote pyrite flotation [4]. Creosotes and pine oils are essentially absolute and have collecting properties not only for coal but also for gangue minerals.

The newer glycol frothers offer an advantage in floating coarse coal particles. Frothers must be added before collectors as prior additions of oil, which mitigates the problem by blocking coal surface to frother adsorption.

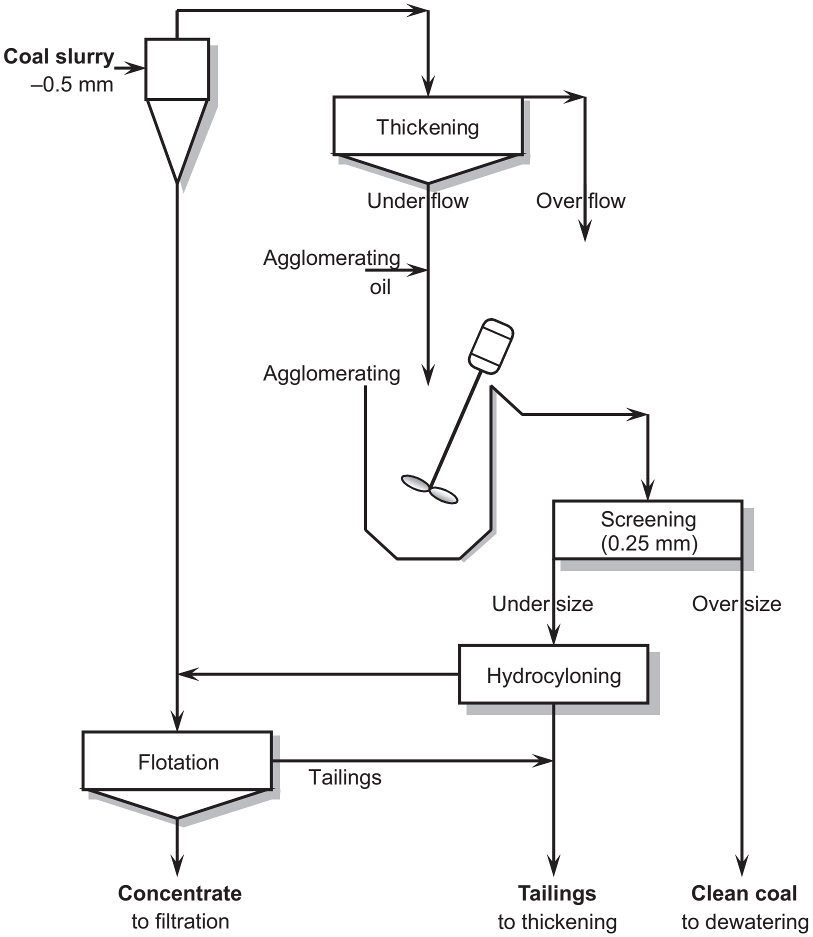


FIGURE 39.5

Olifloc process flow sheet.

Collectors: In coal flotation, the principal function of collectors is to improve hydrophobicity and hence the flotability of coal particles, and at the same time, to be selective toward gangue minerals. The most commonly used collectors for coal flotation is No. 2 fuel oil, for the reason of its effectiveness and cost.

Kerosene is used to the lesser extent, with other collectors. Collector use is required for the flotation of low-rank and oxidized bituminous coal. Based on research studies [3], the advantages and disadvantages of using fuel oil as a collector are shown in Table 39.4.

Depressants: In some instances, it may be desirable to float a pyrite and/or ash mineral and depress coal. A large number of depressants have been examined in various studies. It has been concluded that a dextrin (corn, wheat, tapioca) is an effective

Table 39.4 Summary of Advantages and Disadvantages of Using Fuel Oil as Collector during Coal Flotation

Advantages	Disadvantages
Increases flotation rate of coal	Promotes flotation of pyrite and ash minerals
Increases flotation of low-rank and oxidized coal	Encourages the flotation of all fines (−100 mesh) particles
Floats less hydrophobic particles (e.g., fusinite)	Floats fusinite and carbonaceous shells
Floats coarse particles	Floats locked particles
Serves as a frother extender	
Blocks coal surface against frother adsorption	

coal depressant. Some polysaturates were also used as coal depressants during pyrite flotation. Concerning pyrite depression during coal flotation, the use of ferric chlorite is practiced in some operating plants.

39.3.6 Coal flotation flow sheets used for treatment of various coal ores

There are many variations of coal flotation circuits as there are coal types to be upgraded. In actual fact the flotation circuit design is a function of the type of impurities in a coal-containing ore. The following ore flow sheet is designed for various ore types [5].

Flow sheet for treatment of low pyrite and/or oxidized coal.

The flow sheet used in the treatment of low pyrite and oxidized coal (Figure 39.6) is designed to separately float coarse and fine coal. The important operating factor is that the pulp density in a coarse coal circuit be maintained at about 15% solids while, during fine coal flotation, the pulp density should be maintained at 6% solids. The low pulp density flotation improves rejection of clay particles. Pulp conditioning with reagents prior to the flotation stage improves flotation rate and reduces the level of reagent consumption.

Flow sheet for treatment of high pyrite ore.

The flow sheet used for the treatment of high pyrite ore is similar to that used for the treatment of low pyrite ore except that the cleaning circuit for both coarse and

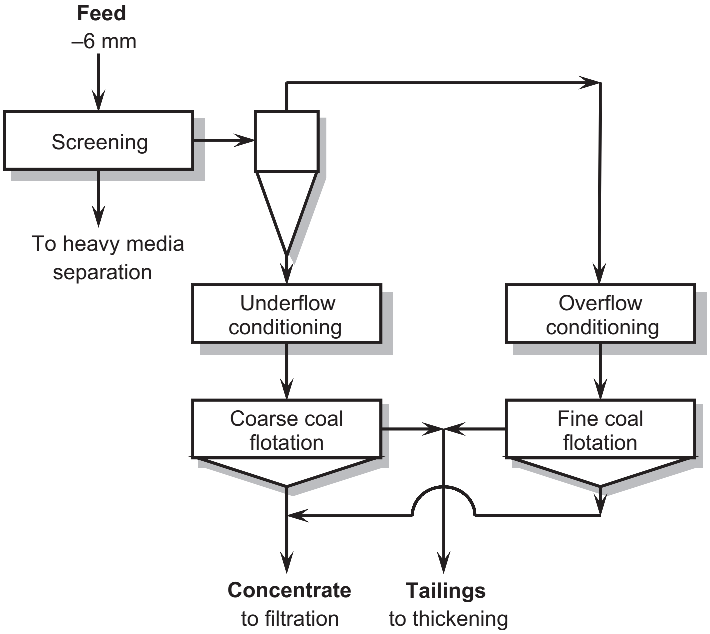


FIGURE 39.6

Flotation circuit design for treatment of low pyrite and/or oxidized coal.

fine coal flotation is added. An extra conditioning stage is also added to the circuit. A first conditioner is used to add pyrite depressant, usually ferric chloride, and the second conditioner to add coal flotation reagents. This flow sheet is shown in Figure 39.7. It should be noted that ferric chloride is an effective pyrite and does not affect flotability of coal.

Flow sheet design for processing of strip coal with high pyrite and high clay.

The flow sheet incorporated attrition scrubbing which was found to be advantageous. The attrition scrubber removes clay from the surface of the coal particles followed by clay removal by cycloning. The flow sheet does not require split circuit flotation of coarse and fines. Again, ferric chloride is used for pyrite depression during coal flotation. This flow sheet is presented in Figure 39.8.

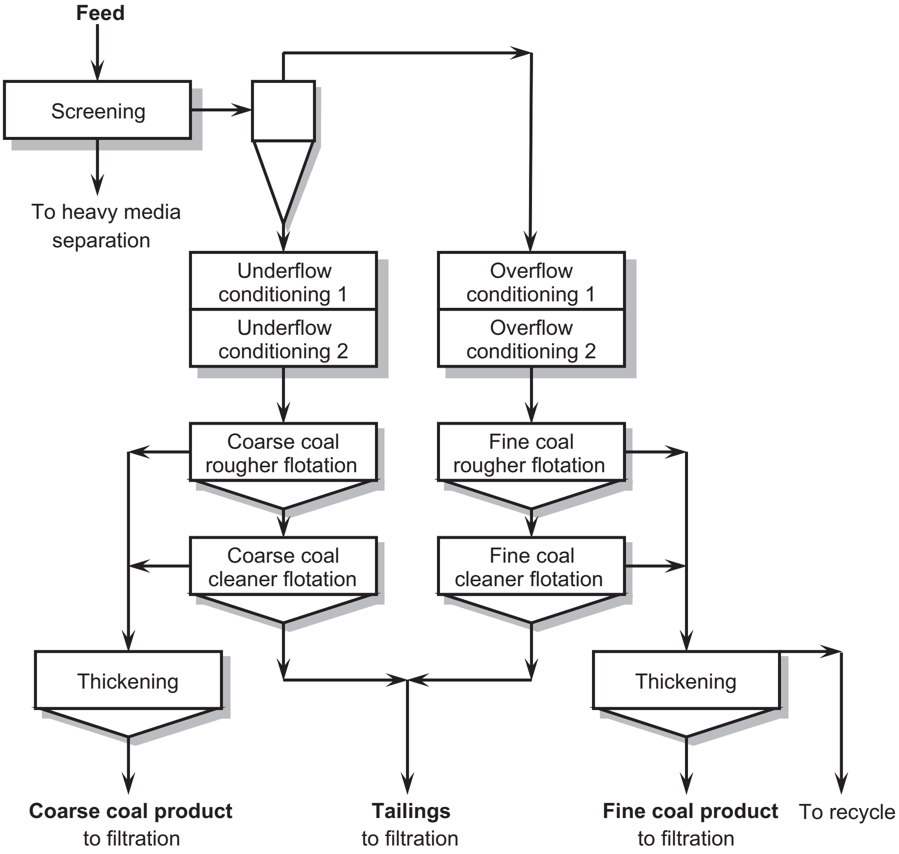


FIGURE 39.7

Flow sheet used in treatment of high pyrite coal.

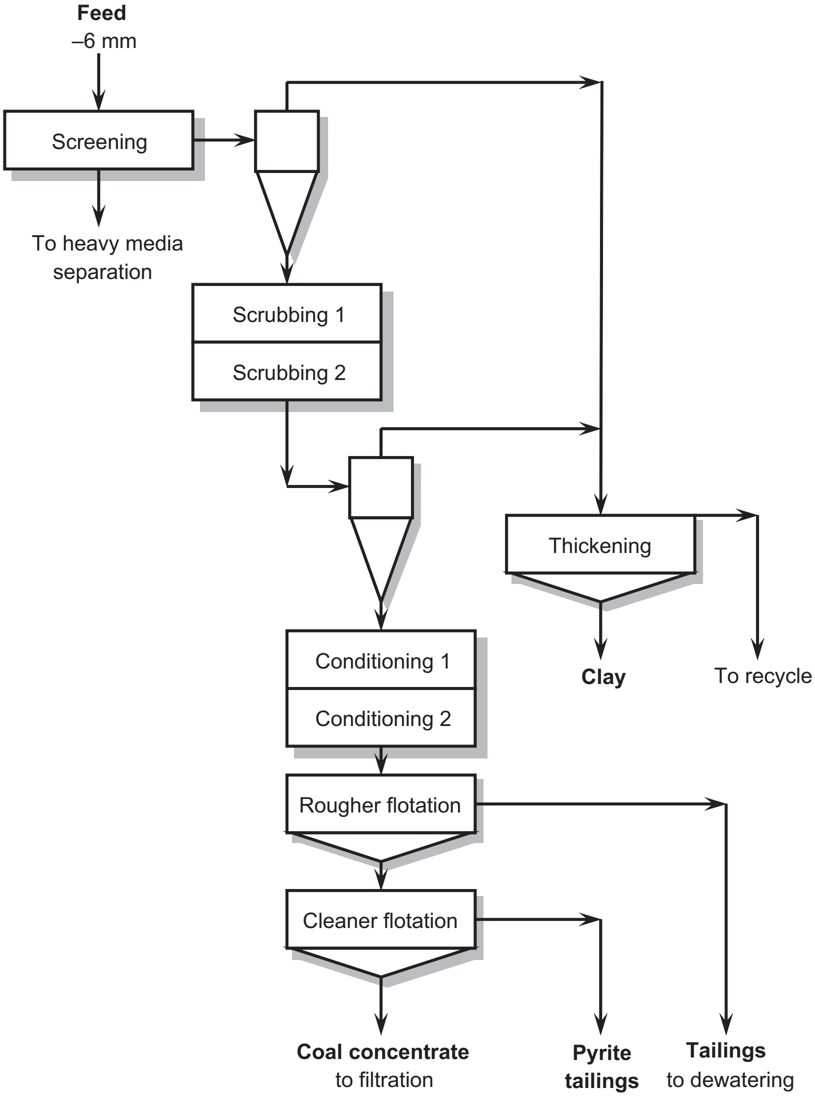


FIGURE 39.8

Flow sheet design for processing strip coal with high pyrite and high clay.

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CHAPTER

Beneficiation of Pollucite Containing Ore

40

CHAPTER OUTLINE

40.1 Introduction

Pollucite mineral is a carrier of cesium and is found along with lithium, feldspar, mica, and the other silicates. Pollucite is an aluminosilicate mineral with variable composition and color.

Beneficiation of pollucite depends on a number of factors including:

- ore mineralogy;
- amount of impurities in the pollucite minerals; and
- liberation profile of pollucite and associated minerals.

In various research work, two beneficiation methods were developed including:

1. direct pollucite flotation; and
2. reverse associated mineral flotation.

A large portion of research work on beneficiation of pollucite was performed by Russian researchers [1–3] working on relatively low-grade pollucite ore.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00040-3

Table 40.1 Cesium Containing Minerals

Mineral	Formula	% Cs_2O Content
Pollucite	$Cs[AlSi_2O_6]H_2O$	30–32
Rhodozite	$KNaLi_4Be_3B_{10}O_{27}$	5–10
Carnallite	$MgCl_2KCl \cdot 6H_2O$	–
Avorgadrite	$(KCs)BF_4$	5–15

Table 40.2 Chemical Composition of Pollucite

	Assays %	% Cs_2O Content
Element	(1) Minimum Value	(2) Maximum Value
SiO_2	46.3	46.3
Al_2O_3	15.8	16.2
Na_2O	2.2	2.1
K_2O	<0.1	<0.1
Rb_2O	0.3	Nil
Cs_2O	33.4	34.7

40.2 Principal minerals of cesium

Table 40.1 shows the cesium containing minerals.

Pollucite is the most abundant and the most important of all cesium minerals. As a mineral, it has a glossy color and is usually associated with lithium minerals.

Rhodozite contains significant quantities of cesium along with rubidium. It belongs to orthoborates. The mineral is relatively rare.

Carnallite contains cesium and rubidium up to 1%.

Avorgadrite is also a rare mineral and may contain up to 15% cesium.

In general pollucite is a principal mineral for the production of cesium. Chemical composition of pollucite is given in Table 40.2.

40.3 Cesium containing deposits

The main deposits that contain cesium are pegmatites of the sodium–lithium type. Such deposits are found in (1) Bernic Lake, Canada; (2) Bikita, Zimbabwe; and (3) Karibib, Namibia. These three deposits contain approximately 500,000 tonnes of cesium. Other less important deposits are:

- tantalum-bearing lithium fluorine granites;
- beryllium-bearing greisen deposits; and
- feldspar metasomatites.

Pollucite most commonly occurs in the form of irregularly shaped nests reaching 18 mm in thickness. These nests occupy spaces between segregation of microcline, spodumene, early quartz, amblygonite, and petallite.

This is important to know from the beneficiation point of view.

40.4 Beneficiation of pollucite

40.4.1 General consideration

Commercial flotation process for the recovery of pollucite exists mostly in Russia due to low-grade ore (i.e., 5% Cs_2O). In contrast, the literature and research work for beneficiation of pollucite is abundant.

In some operating plants in Russia, a concentrate grade of 10–15% Cs_2O was produced from the ore containing 0.5–0.7% Cs_2O, using direct flotation of pollucite.

40.4.2 Flotation properties of pollucite

From the research studies [4–6] the flotation properties of pollucite are similar to those of albite, spodumene, and microcline. The crystallographic structure and the ability for pollucite to exchange specific cations differ from those of other minerals with similar structure. This can be utilized for selective flotation of the pollucite from other minerals.

For example, pollucite can be effectively depressed by fluorites (i.e., NaF, HF, etc.), while albite and microcline can be effectively floated in which case the reverse flotation technique is utilized.

The effect of H_2SiF_6 on flotation of pollucite and associated minerals is presented in Figure 40.1.

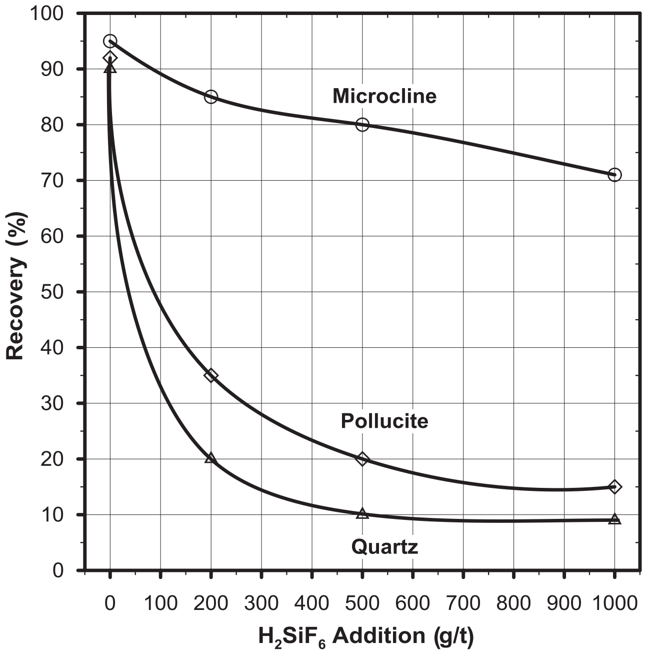

FIGURE 40.1

Effect of H_2SiF_6 on flotation of different minerals using aminonitroparaffin as a collector.

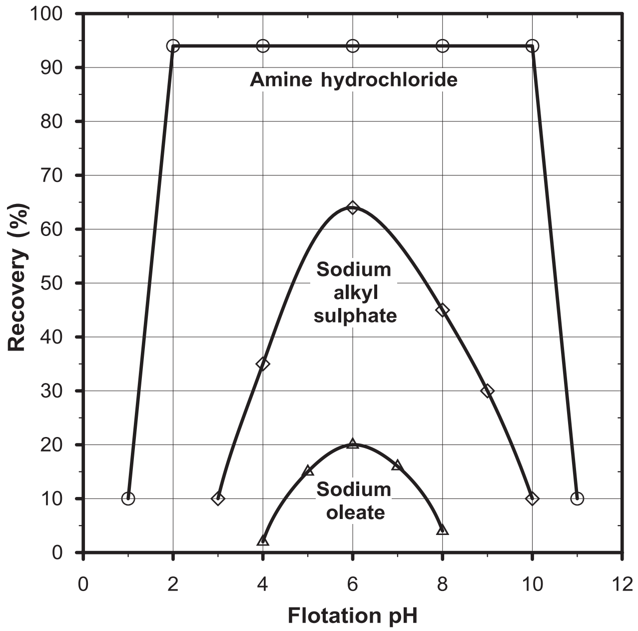

FIGURE 40.2

Effect of pH on pollucite flotation using different collectors.

Pollucite responds poorly to flotation with fatty acids and sodium oleate. Figure 40.2 shows the effect of pH on pollucite flotation with different collectors. This can be utilized to recover spodumene ahead of pollucite using fatty acid.

Good pollucite flotation was achieved using amine hydrochloride with an average carbon chain length of 14C.

40.4.3 Research and development on flotation of pollucite

There are three major methods developed for beneficiation of pollucite. These include:

- reverse flotation technique;
- direct flotation of pollucite; and
- stage sequential flotation.

Each of the above methods is described in the following sections.

40.4.3.1 Reverse flotation technique

A reverse flotation technique as described in a US Patent involves reverse flotation of albite and muscovite while depressing pollucite. Table 40.3 (a) and (b), shows test conditions and results obtained using reverse a flotation technique.

Table 40.3 Flotation Test Conditions and Results Using Reverse Flotation Technique

	Reagent Additions g/t		pH	
Reagent	**Roughers**	**Cleaners**	**Rougher**	**Cleaner**
(a) Conditions				
Depressants + Modifiers				
H_2SO_4	2500	800	2.0	2.0
HF	1200	950	–	–
$Al_2(SO_4)_3$	250	–	–	–
Collector			–	–
Armac CD	750	160	–	

		Assays %				% Distribution	
Product	**Wt%**	**Cs**	**Rb**	**K**	**Na**	**Cs**	**Rb**
(b) Results							
Combined cleaner concentrate	63.7	1.70	0.217	–	–	13.4	82.1
Combined rougher + Cl. tails	36.3	20.4	0.068	0.26	3.88	86.6	17.9
Head (calc.)	100.00	8.54	0.16	1.40	4.92	100.0	100.0

In this case pollucite was depressed using HF and $Al_2(SO_4)_3$ and albite, muscovite were floated using coco amine acetate (ArmacCD).

In these experiments, the ground ore is stage conditioned followed by rougher flotation. The rougher concentrate was cleaned three times.

Another reverse flotation method from the ore containing microcline quartz and pollucite involves pollucite depression using H_2SiF_6 as a pollucite depressant and floting microcline and quartz using collector amine hydrochloride. Figure 40.3 shows the effect of pH on flotation of pollucite, microcline, and quartz.

It has been stated that with depression of pollucite and flotation of accompanying minerals, a high level of dissolution of anions occurs resulting in complete depression of pollucite while microcline and quartz was not affected at a pH region of 6–7. Reagent consumption in these experiments was 700 g/t H_2SiF_6 and 300 g/t collector. The flotation pH was 2.5.

40.4.3.2 *Direct flotation of pollucite*

Direct flotation of the pollucite method is used from the ore that contains spodumene and quartz. In these experiments, pollucite was floated using amine hydrochloride at a pH of 2–2.5.

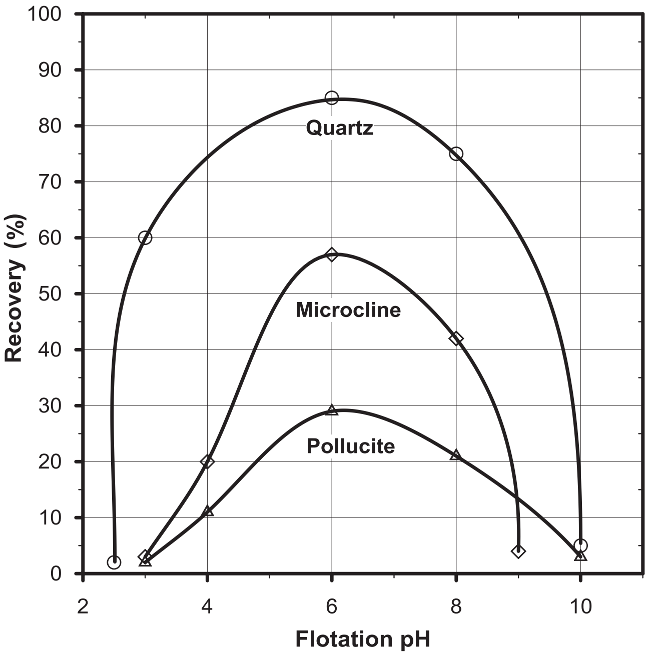

FIGURE 40.3

Effect of pH on flotation of pollucite microcline on quartz using collector amine hydrochloride.

The tailing from the pollucite flotation is thickened followed by spodumene flotation using fatty acid at pH 8.5 controlled by NaOH. Using direct pollucite flotation, a concentrate grade of 15% CsO_2 was achieved at the recovery of 85% CsO_2.

40.4.3.3 Stage sequential flotation

Stage sequential flotation was developed by Russian scientists [7,8]; stage sequential flotation was performed on the ore containing spodumene, beryl, feldspar, tantalum, and silicate.

Initially tantalum was recovered using gravity followed by spodumene flotation using fatty acid in alkaline pH. From the spodumene tailing, soda and potassium feldspars are recovered. The feldspar tailing was thickened followed by pollucite flotation using amine hydrochloride, followed by beryl flotation. The resulting tailing was silica.

Metallurgical results obtained using stage sequential flotation are presented in Table 40.4.

Table 40.4 Metallurgical Results Obtained Using Stage Sequential Flotation

Product	Wt%	Assays %					% Distribution				
		Cs_2O	Li_2O	Rb_2O	Ta_2O_3	BeO	Cs_2O_5	Li_2O	Rb_2O	Ta_2O_3	BeO
Ta_2O_5 concentrate	0.09	–	–	–	32	–	–	–	–	53.5	–
Li_2O concentrate	13.42	–	5.8	–	–	–	–	59.0	–	–	–
Li_2O middlings	4.2	–	–	–	–	–	–	–	–	–	–
K-feldspar concentrate	7.8	–	–	3.0	–	–	–	–	33.0	–	–
Na-feldspar concentrate	28.5	–	–	0.9	–	–	–	–	36.5	–	–
Beryl concentrate	0.35	–	–	–	–	5.1	–	–	–	–	35.3
Cs_2O concentrate	7.5	8.5	–	–	–	–	58.0	–	–	–	–
Middlings	0.6	–	–	–	–	–	–	–	–	–	–
Tailing	27.5										
Slimes	14.8										
Head	100.0	14.1	1.32	0.7	0.054	0.056	–	–	–	–	–

40.5 Concluding remarks

- A large portion of research work on pollucite beneficiation using the flotation technique was done by Russian scientists.
- In the past two decades significant progress has been made on beneficiation of pollucite, yet only commercial operation exists in Russian treating low-grade pollucite ore.
- The new flotation methods developed so far are quite effective.

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CHAPTER

Beneficiation of Iron Ores 41

CHAPTER OUTLINE

41.1 Introduction

Development and operating status of the flotation processes are relative to the nonmagnetic iron ores. The interest in the iron ore flotation began in the late 1930s and continues to the present day. There are several processes developed for the beneficiation of iron ores. These include:

- magnetic separation that applies to the ores that contain magnetite;
- reverse silica flotation that applies to the nonmagnetic ores (i.e., hematite and martite);
- direct nonmagnetic iron flotation and depression of silica minerals; and
- combination of nonmagnetic ore flotation on silica or apatite flotation.

In a number of cases, the combination of magnetic separation and silica flotation from magnetic concentrate is practiced.

In the treatment of disseminated nonmagnetic iron ore beneficiation, a combination of selective flocculation reverse silica flotation is practiced.

Handbook of Flotation Reagents: Chemistry, Theory and Practice. http://dx.doi.org/10.1016/B978-0-444-53083-7.00041-5

41.2 Iron ore deposits and minerals

There are numerous iron ore deposits and operating plants around the world (i.e., Australia, China, Russia, Africa, South America, U.S., and Canada). There are a variety of deposit types some of which include:

- *Sedimentary deposits* of a Middle Precambrian volcano iron formation. These ore bodies consist mainly of oxide faces. Sometimes these deposits have been regionally metamorphosed to staurolite grade. These deposits contain magnetite and hematite.
- *Bedded clastic deposits* with distinct formation. In these deposits, ore minerals tend to be coarse from 28 to 200 mesh and consists mainly of quartz, hematite, and magnetite. The hematite-to-magnetite ratio varies from all hematite, to about 75% magnetite.
- *Banded oxide*—facies, iron formation deposits. Carbonate, silicate sulfides, and mixed facies members are present and are the dominant host rock of some ore bodies. The high-grade nonmagnetic iron ore deposits are highly weathered and enriched in iron. These ores are typically banded, friable, and porous masses that are generally classified by color: (1) "blue ore"are remnants of oxide facies units and consist mainly of martite; (2) hematite and magnetite; (3) "yellow ore" are remnants to silicate and mixed silicate–carbonate facies and consist mainly of goethite and limonite; and (4) "red ore" are composed mainly of fine grained soft red hematite.
- *A brecciated porphyry iron ore deposit*, where iron occurred principally as open space filling. The ore and the enclosing rocks are Precambrian age. Hematite constituted 80–95% of the iron oxide and magnetite made up the remainder. Gangue minerals are generally coarse grained and consist mainly of andradite, garnet, quartz, calcite, apatite, dolomite, fluorite, and barite.
- *Oxidized taconite iron ore deposits* occurred in the U.S. Minnesota region and represent oxidized products of original magnetite and for carbonate silicate reach units of the Middle Precambrian Biwabik iron formation. The ore is composed principally of goethite, hematite, and martite. The principal iron ore minerals are magnetite, hematite, and martite. There are a number of iron ore deposits of different origins, which depend on the regions (i.e., Russia, Australia, North America, etc.).

41.3 Physical beneficiation method

Two principal physical separation methods exist. These apply (refer) to beneficiation methods of iron ore applied in practice. These include: (1) magnetic separation and (2) gravity concentration.

- *Magnetic separation* is applied on the ores that contain primarily magnetite. The concentrate grade using this method ranges from 60% to 68% Fe and 5–9% SiO_2. In some cases, using this method, concentrate contains appreciable amounts of P_2O_5 and CaO, which is an unwanted impurity. These can be removed by flotation, which will be discussed in this chapter. A typical flow sheet is relatively simple and involves grinding, desliming, and primary and secondary magnetic separation. Concentrates are reground and recleaned using a magnetic separator provided that the concentrate contains middlings.

- *Gravity separation* is applied on nonmagnetic iron. Typically, spirals are used to produce concentrate assaying 60–62% Fe and 7–9% SiO_2. In practice, a combination of gravity concentration and flotation is used.

41.4 Flotation beneficiation method

41.4.1 Research and development

The operations of very large deposits that contain finely disseminated ore and considerable amounts of nonmagnetic iron, makes flotation more and more attractive as a method of concentrating iron ores. Even the magnetite concentrate derived by magnetic separation sometimes contains high silica and other impurities (i.e., CaO, P_2O_5) that need to be removed using the flotation method. The first research into iron flotation in the U.S.S.R and elsewhere dates back to over 50 years ago [1–3] and extensive development and in-plant application began recently and continues nowadays. The first commercial plants were put in operation in U.S.S.R., China, and U.S.

There are two principal methods used in iron ore beneficiation using the flotation method. These are:

- silica flotation and iron depression (i.e., nonmagnetic iron); and
- nonmagnetic iron flotation and depression of silicate.

The use of the either method largely depends on the mineral composition of the ore. For example, if the ore contains more iron than silicate, then silica flotation is used. Other factors that dictate selection of the flotation method is the presence of calcite and phosphate, which must be removed using the flotation method.

41.4.1.1 Selective flotation of silicates from iron ore

For the flotation of silicate from iron minerals, a number of methods have been proposed: (1) hydrated lime method [4], (2) caustic-metaphosphate method [5], and (3) caustic lignin method. Using these methods anionic collectors were used.

The iron ore depressants during cationic flotation of silicate include starches, dextrins, lignins, and phosphates.

The pH control during silica flotation is done by NaOH. The flotation pH range is between 8.0 and 10.1.

Typical results obtained using amine collectors (MG83-AKZO Nobel) are shown in Table 41.1.

In these experiments NaOH was used for pH control and Dextrin (WW-82) was used for iron depression. Other iron depressants studied included use of chelating reagents in EDTA and 1.8 diamino octane. The grade recovery curve using different levels of 1.8 diamino octane are shown in Figure 41.1.

In these experiments silica flotation was performed using the diamino collector.

Most recently, a reagent scheme was developed in which causticized starch was used as an iron depressant and an amine collector (D-17) was used for silica

Table 41.1 Metallurgical Results Obtained Using Amine Flotation

		Assays %		Distribution %	
Product	**Wt %**	**Fe**	**SiO_2**	**Fe**	**SiO_2**
Ore feed	100.00	56.0	13.7	100.0	100.0
Tailing (froth product)	16.5	20.1	65.3	5.9	–
Concentrate (cell product)	83.5	63.1	3.5	94.1	–

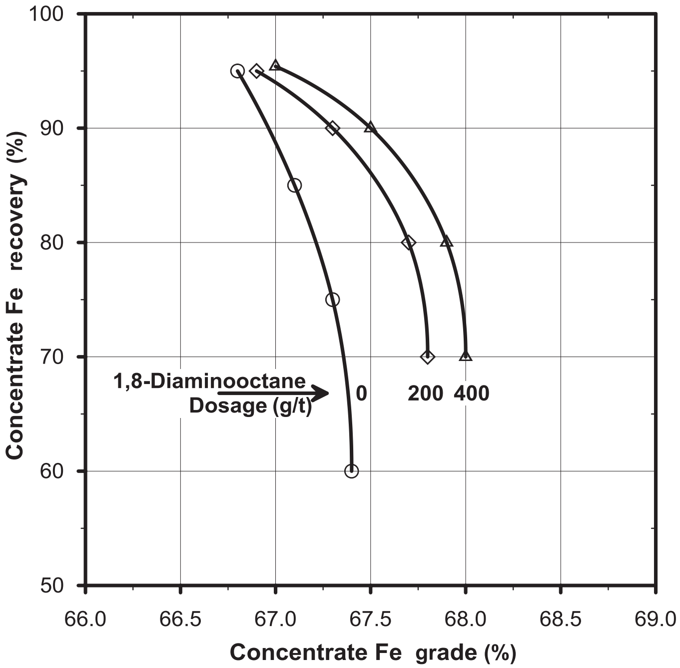

FIGURE 41.1

Typical grade recovery relationship using different levels of 1.8 diamino octane.

flotation. Metallurgical results obtained in a continuous laboratory test are shown in Table 41.2 [6].

Excellent iron depression was achieved using caustic starch. Using amine D-17, silica floted relatively fast.

The level of caustic starch had some effect on iron losses in a silica concentrate. Figure 41.2 shows the effect of the level of caustic starch on iron recovery.

Another iron depressant that showed good iron depression during amine silica flotation was wheat dextrin of industrial grain product. The results obtained using wheat dextrin (i.e., 500 g/t) are summarized in Table 41.3.

Cationic flotation of silica. This method is used when the ore contains calcite and phosphate. In this case, both calcite and phosphate can be recovered using fatty

Table 41.2 Metallurgical Results Obtained Using Caustic Starch and Amine D-17—Ferrous Resources, Brazil

Product	Wt%	Assays %			% Distribution	
		Fe	SiO_2	P_2O_5	Fe	SiO_2
Fe concentrate (cell tail)	46.45	63.2	3.1	0.025	93.5	5.1
SiO_2 Cl. concentrate (froth)	53.55	3.81	49.7	0.16	6.5	94.9
Feed	100.0	31.4	28.1	0.15	100.0	100.0

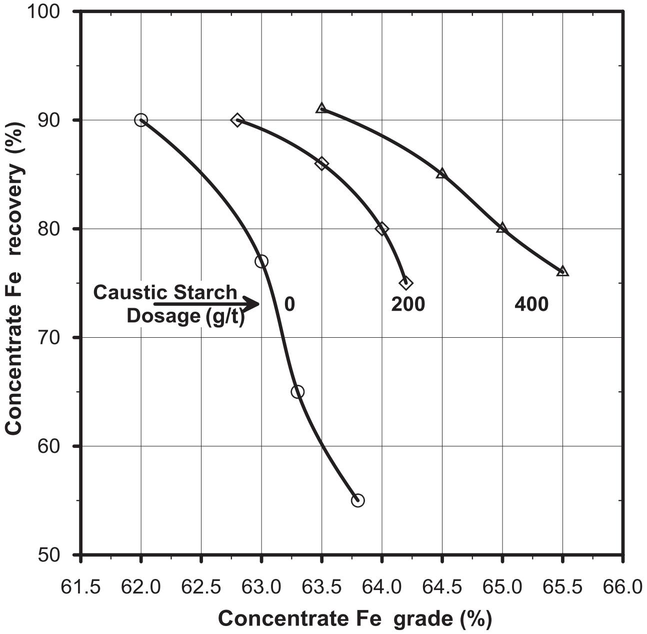

FIGURE 41.2

Effect of level of caustic starch on iron grade recovery relationship.

acid. Normally when using a fatty acid collector, a silica activator is used due to the fact that flotability of silica without the presence of an activator is relatively poor. Calcium chloride and related compounds were effective silica activators using fatty acid as a silica collector.

An example of the results obtained using fatty acid and an activator are shown in Table 41.4.

In these experiments the following reagents were used.

$NaOH = 250$ g/t
$Ca(OH)_2 = 2500$ g/t
$Na_2CO_3 = 300$ g/t

Table 41.3 Effect of Wheat Dextrin on Amine Silica Flotation

Product	Wt%	Assays %		Distribution %	
		Fe	SiO_2	Fe	SiO_2
Fe concentrate (cell product)	79.2	62.9	4.5	93.2	20.1
SiO_2 concentrate (froth tail)	20.8	17.4	67.4	6.8	79.9
Feed	100.0	53.4	17.4	100.0	100.0

Table 41.4 Effect of Fatty Acid on Silica Flotation Using Fatty Acid Collector in the Presence of Activator

Product	Wt%	Assays %		Distribution %	
		Fe	SiO_2	Fe	SiO_2
Fe concentrate (cell product)	85.0	62.4	3.3	95.2	–
SiO_2 concentrate (froth tail)	15.0	17.8	74.9	4.8	–
Feed	100.0	55.8	14.0	100.0	–

Chloride sulfonate = 1200 g/t
Acintol FA-2 = 800 g/t
WW-82 = 450 g/t

The use of lime during silica flotation aids iron depression during silica flotation.

Flotability of silica using the activator $CaCl_2$ is dependent on pH. Figure 41.3 shows the silica hematite recovery relationship as a function of pH.

Maximum silica recovery was achieved at pH 9.0. While at pH below 7, no silica flotation was evident. When using fatty acid silica flotation on the ore that contained calcite and phosphate, most of the calcite and phosphate reports to the silica concentrate. Testwork conducted on several ore samples using amine and fatty acid silica flotation showed substantial reduction of calcite and phosphate in the iron concentrate when using fatty acid as compared to amine flotation.

Table 41.5 compares the results obtained using fatty acid and amine collector.

Ore samples used in this testwork were crude ore from Cleveland Cliff US operation.

Fatty acid silica flotation has been practiced in a number of Russian operating plants.

Another method that is examined involves selective flocculation followed by silica flotation. In a selective flocculation, a large portion of fine silicate and other gangue is removed followed by the remaining silica flotation, using either amine or fatty acid.

Starches or cross-linked starches were used in selective flocculation. The pH in the selective flocculation is maintained between 10 and 10.5 sodium silicate or phosphate is used as a dispersant. In the selective flocculation process lime is used in some cases [7]. The additions of lime in this process have three functions: (1) it

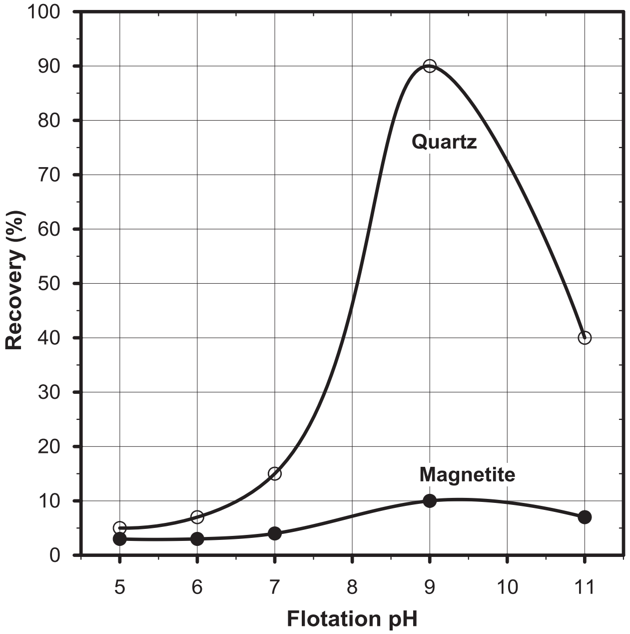

FIGURE 41.3

Effect of pH on recovery of quartz and magnetite using $CaCl_2$ and 8-diamine collector.

Table 41.5 Effect of the Type of Collector on Calcite and Phosphate Content of Iron Concentrate

	Assays %							
	Fatty Acid Flotation				Amine Flotation			
Sample No.	Fe	SiO_2	CaO	P_2O_5	Fe	SiO_2	CaO	P_2O_5
33A	63.3	4.2	0.11	0.02	63.3	4.1	2.8	0.1
40B	62.8	5.1	0.10	0.03	63.1	4.8	3.1	0.12
44A	63.8	4.0	0.08	0.02	63.3	3.9	2.1	0.10
48B	64.1	3.3	0.07	0.025	63.8	3.6	2.5	0.09

assists the cationic polymer in flocculating the highly dispersed slime; (2) it softens the hard makeup water; and (3) it raises pH of the reclaim water so less sodium hydroxide is required.

Therefore the lime-polymer flocculation reagent system is effectively used in a selective flocculation–flotation method.

41.4.1.2 Selective flotation of nonmagnetic iron from iron containing ore

Extensive research work was conducted by US and USSR researchers on nonmagnetic iron flotation from siliceous gangue minerals. In the studies conducted on Hana

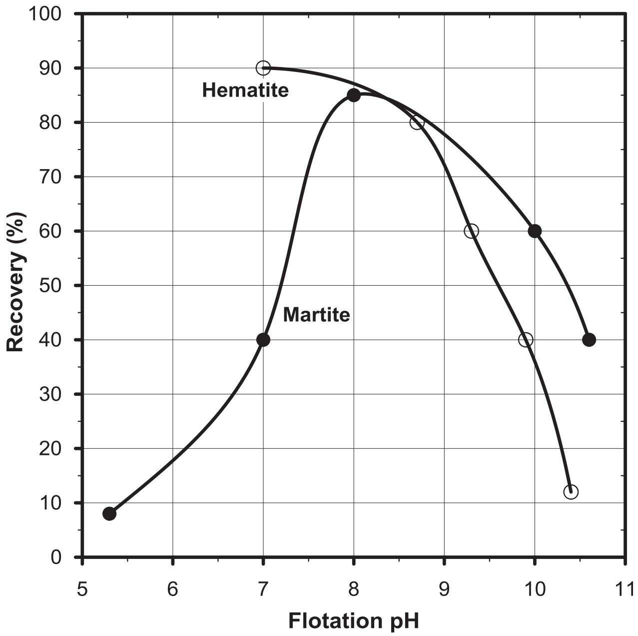

FIGURE 41.4

Effect of pH on hematite and martite flotation using Vetluga oil.

Mining Iron Ore [8] fatty acid collector with low resin content in conjunction with No. 2 fuel oil was used.

The amount of fuel oil used was 3–4 times the fatty acid content. Sodium silicate was used as a silica depressant.

The Russian researchers have developed a reagent scheme consisting of Vetluga oil. The neutral part of Vetluga oil is 50% hydrocarbons of the naphthalene and anthracene series, up to 20% aromatic aldehydes and ketones, and 30% alcohols and ethers. The effect of Vetluga oil on hematite and martite flotation as a function of pH is presented in Figure 41.4 [9].

Maximum nonmagnetic iron flotation was achieved at pH region 7–9.

The Swedish researchers [10] have developed a unique collector for beneficiation of Scandinavian hematite. The collector consists of tall oil and fuel oil emulsified in water by means of an emulsifying agent, generally a water soluble alkylarylsulfonate. The preparation method of emulsion is quite important.

The ratio of tall oil and fuel oil determines the hematite grade recovery relationship. Figure 41.5 shows the effect of tall oil/fuel oil ration on hematite grade recovery relationship.

As the amount of fuel oil to tall oil increases both grade and recovery increases.

This process requires high solids (~65%) and prolonged conditioning time before flotation with a reagent mainly to ensure proper slime control.

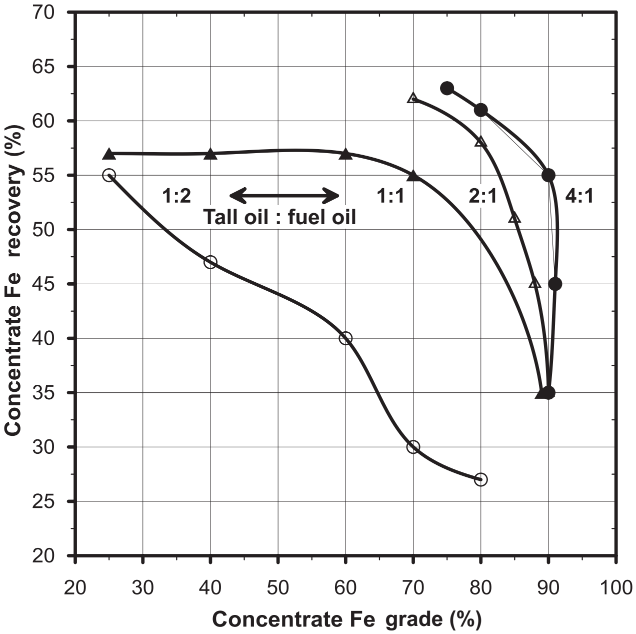

FIGURE 41.5

Effect of tall oil/fuel oil ratio on hematite grade recovery relationship.

Anionic petroleum sulfonate. This method uses petroleum sulfonate from the 800 series (Cytec). Using this method the ore has to be deslimed before flotation. In some cases the iron losses in the slime fraction are relatively high. In this process H_2SO_4 is used for pH control at pH region 3.5–4.5. Under these conditions silica does not float in the presence of petroleum sulfonate, so no silica depressant is used.

When ore contains appreciable amounts of calcite in the ore, it has been found that calcite rejection using the sulfonate method is not effective. A sequential calcite–hematite process has been developed where initially calcite was floated followed by iron flotation using a sulfonate collector. The results obtained [11] are presented in Table 41.6.

In this experiment, both calcite and iron flotation feed were deslimed before flotation. Most of the silica reported to the calcite concentrate.

The reagents used were as follows:

Carbonate Circuit	Iron Circuit
Fatty acid (L-S) = 150 g/t	H_2SO_4 = pH 3.0
Gum 9072 = 200 g/t	Sulfonate R899 = 400 g/t
Fuel oil = 600 g/t	Fuel oil = 60 g/t
NaOH = pH 9.5	Sodium silicate = 300 g/t

Table 41.6 Sequential Calcite–Hematite Pilot Plant Flotation Results

Product	Wt%	Assays %			% Dist.
		Fe	SiO_2	CaO	Fe
Feed	100.0	28.1	41.7	2.1	100.0
Iron concentrate	33.4	62.7	2.07	0.3	73.1
Carbon concentrate	39.0	7.6	67.2	–	10.5
Iron tailings	9.2	8.4	–	–	2.7
Slimes	18.4	21.0	–	–	13.7

41.5 Examples of commercial operation

There are over more than 500 operating plants that treated iron ores. The larger portion of operation treats magnetite ore using exclusively grinding magnetic separation. Other operating plants are using nonmagnetic iron flotation and silica depression ore iron depression and silica flotation.

This section summarized some important operations that treat nonmagnetic ores.

Russian operation. There are a number of Russian operations that treat nonmagnetic iron ore, some of which are disseminated. Several plants are using iron depression and silica flotation using fatty acid with low resin content. Iron depression during silica flotation is achieved using starch ore modified dextrin.

Operating plants that float iron and depress silica ore treating relatively disseminated ore. The ground ore is deslimed followed by stage conditioning with sodium silicate, H_2SO_4 (to pH 3.5), and a collector consisting of modified fatty acid. A concentrate grade of 61% Fe and containing 5–7% SiO_2 at iron recovery of 75–85% was achieved.

Swedish operation. The iron ore treated in Sweden is a mixture of hematite and apatite. During extensive development testwork, a flow sheet consisting of sequential apatite and hematite flotation has been developed. Initially apatite is floated using a sarcosine collector type followed by hematite flotation using an emulsion consisting of tall oil:fuel oil in a ratio of 1:2. In the hematite circuit, sodium silicate was used as a silica depressant. Figure 41.6 shows the flow sheet used in a sequential apatite hematite flotation.

United States operation. Major iron operations are located in Northeast United States (Minnesota) that treat taconite ores.

1. Mesabi semitaconite operation treats semitaconate ore assaying 38.9% Fe and 31.1% SiO_2. The ore is composed of quartz, goethite, hematite, and a minor amount of magnetite. The ore is ground to 75% ‘325 mesh before flotation. From this ore silica is floated using fatty acid and iron was depressed with guar 907. The flotation pH ranges between 10.5 and 11.0. A generalized flow sheet is shown in Figure 41.7.
2. *Groveland plant* treats ore that contains magnetite and hematite. The flow sheet includes magnetic separation followed by hematite flotation using petroleum sulfonite collectors in acid pH = 3.5. The plant flow sheet is shown in Figure 41.8.

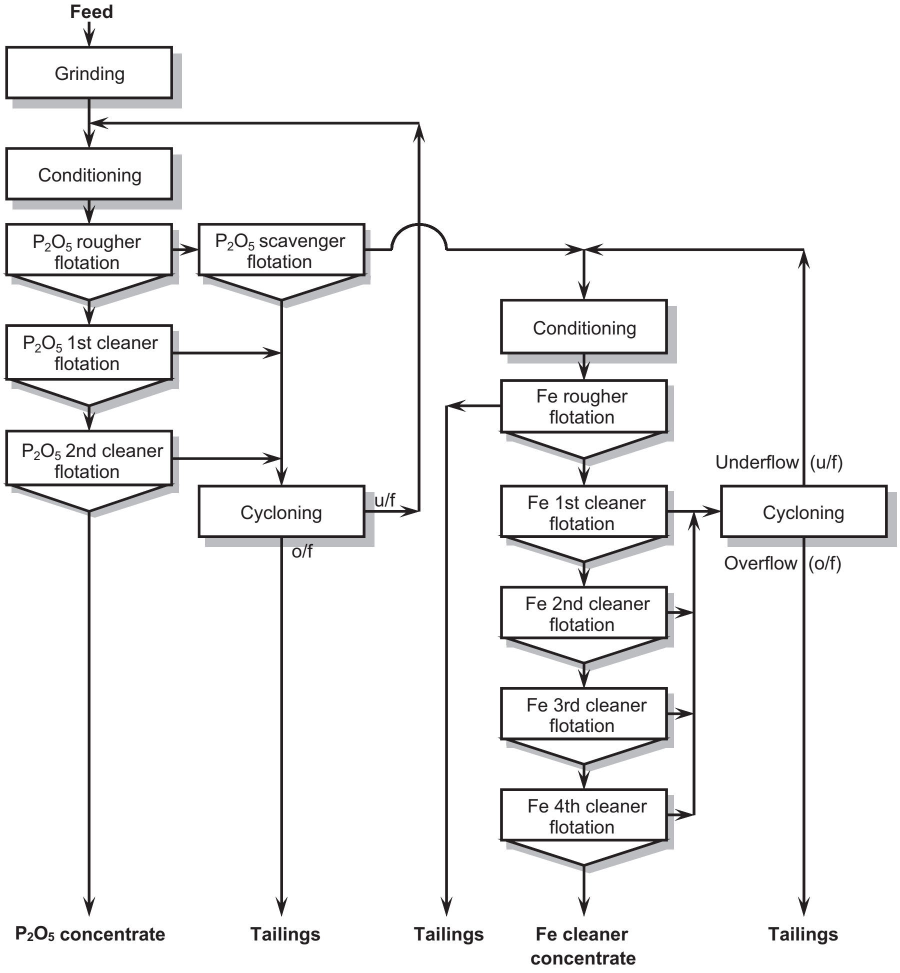

FIGURE 41.6

Flow sheet used in sequential apatite hematite flotation.

3. *Tilden operation, Michigan, US* treats disseminated ore containing mainly martite–hematite. The ore is ground to about 85% minus 25 μm before flotation. The treatment process involves selective flocculation–flotation using cationic silica flotation. A concentrate grade assaying 65% Fe at 4.85% SiO_2. The iron recovery ranges from 80% to 85% Fe.

The average metallurgical results obtained are shown in Table 41.7.

The ore contains a minor amount of phosphate, which reduces the quality of pellets. The plant test showed that use of a long chain polyphosphate portion of apatite is rejected in flocculation desliming stage.

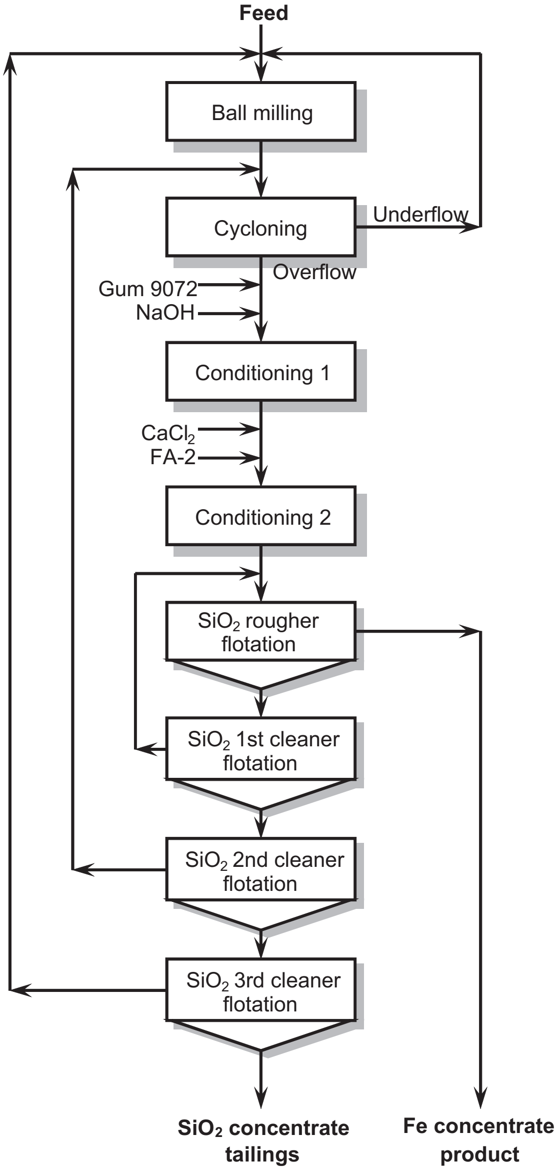

FIGURE 41.7

Mesabi flow sheet for beneficiation of semitaconite ore.

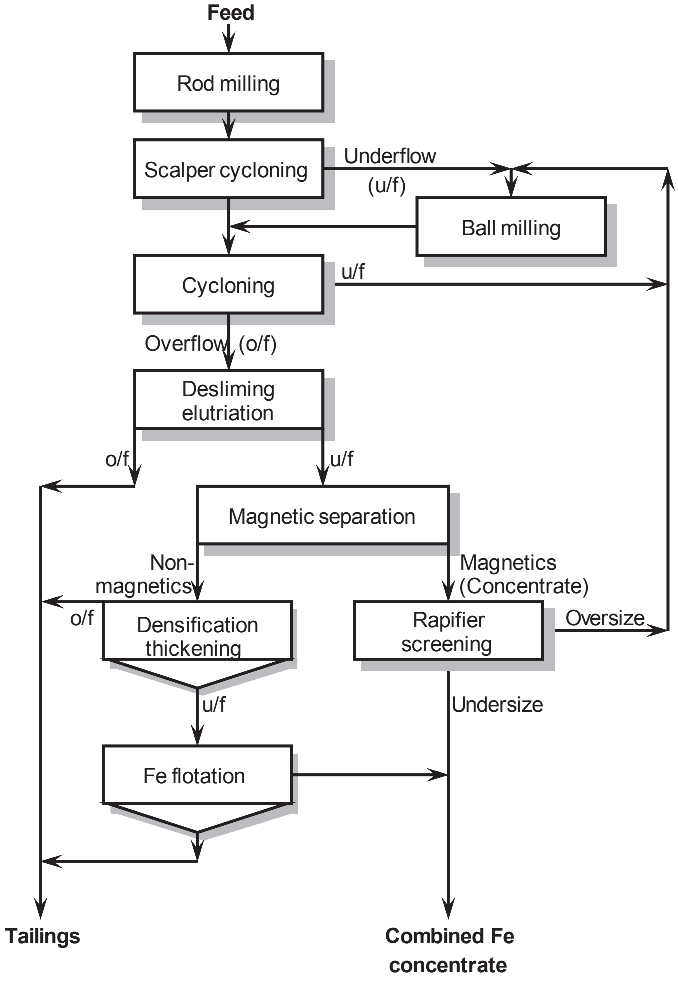

FIGURE 41.8

Groveland plant flow sheet using magnetic separation flotation.

Table 41.7 Mesabi Metallurgical Results

		Assays %		% Distribution
Product	**Wt%**	**Fe**	**SiO_2**	**Fe**
Feed	100.0	38.9	39.1	100.0
Fe concentrate (cell tailing)	58.4	60.3	5.9	90.5
SiO_2 concentrate (froth product)	41.6	8.9	-	9.5

41.5.1 Canadian operations

1. *Sept-Iles beneficiation plant* is located in Quebec, Canada. It treats siliceous hematite ore with relatively high-grade hematite. The plant reagent scheme involves silica flotation and depression of iron. The plant flow sheet is shown in Figure 41.9.

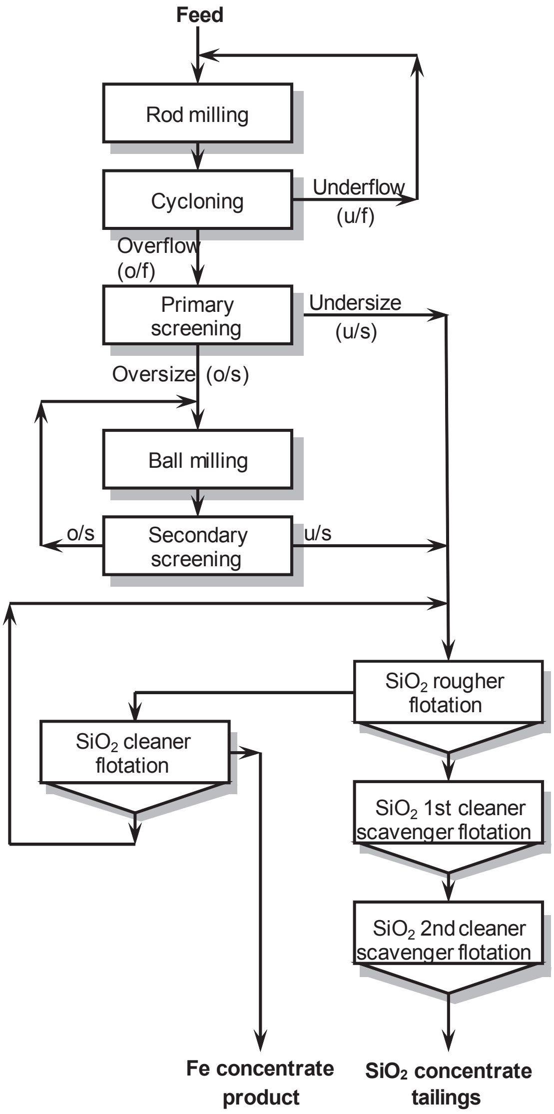

FIGURE 41.9

Sept-Iles plant flow sheet.

Metallurgical results obtained are shown in Table 41.8.

The following reagents and quantities are used:

NaOH = 450 g/t (pH 9.5)
Dextrin (WW-82) = 400 g/t
Amine MG82 = 120 g/t
Frother = 30 g/t

2. *Iron ore of Canada* treats magnetite-containing ore using magnetic separation [12]. Concentrate assay 62% Fe with 6.5% SiO_2 is produced. Research work was conducted in an attempt to produce concentrate with low silica content. Using ether amine and modified linoleic acid, the silica content of the iron concentrate was reduced to 0.2% SiO_2. Metallurgical results obtained are shown in Table 41.9.

Table 41.8 Plant Metallurgical Results

		Assays %		% Distribution
Product	**Wt%**	**Fe**	**SiO_2**	**Fe**
Feed	100.0	56.0	13.7	100.0
Fe concentrate (cell tailing)	83.5	63.1	3.5	94.1
SiO_2 concentrate (froth product)	16.5	20.1	65.3	5.9

Table 41.9 Continuous Locked Cycle Test Results Obtained on Silica Flotation from Magnetic Concentrate

		Assays %		% Distribution
Product	**Wt%**	**Fe**	**SiO_2**	**Fe**
Feed (magnetic concentrate)	100.0	62.0	6.5	100.0
Fe concentrate (cell tailing)	–	66.1	0.25	97.5
SiO_2 concentrate (froth product)				

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