Kirk-Othmer Encyclopedia of Chemical Technology.

FLOTATION

Flotation or froth flotation is a physicochemical property-based separation process. It is widely utilized in the area of mineral processing also known as ore dressing and mineral beneficiation for mineral concentration. In addition to the mining and metallurgical industries, flotation also finds applications in sewage treatment, water purification, bitumen recovery from tar sands, and coal desulfurization. Nearly one billion tons of ore are treated by this process annually in the world. Phosphate rock, precious metals, lead, zinc, copper, molybdenum, and tin-containing ores as well as coal are treated routinely by this process; some flotation plants treat 200,000 tons of ore per day (see Mineral recovery and processing). Various aspects of flotation theory and practice have been treated in books and reviews (1–9).

1. Technology

The flotation process is based on the exploitation of wettability differences of particles to be separated. Differences of wettability among solid (mineral) particles can be natural, or can be induced by the use of chemical adsorbates. Because the largest segment of industrial applications is conducted in water, with air, the following discussion is confined mainly to these fluids.

The flotation process applies to a particle size range of about 500 μm (eg, coal cleaning) to 2–10 μm (eg, copper ore concentration); however, 65 mesh (230 μm) to 270 mesh (53 μm) is typical. Figure 1 shows the relationship between flotation recovery and particle size in a sulfide ore processing operation and illustrates the optimum range (10). Figure 2 summarizes the main steps in mineral processing using froth flotation.

The raw ROM (run of mine) ore is reduced in size from boulders of up to 100 cm in diameter to about 0.5 cm using jaw crushers as well as cone, gyratory, or roll-type equipment. The crushed product is further pulverized using rod mills and ball mills, bringing particle sizes to finer than about 65 mesh (230 μm). These size reduction (qv) procedures are collectively known as comminution processes. Their primary objective is to generate mineral grains that are discrete and liberated from one another (11). Liberation is essential for the exploitation of individual mineral properties in the separation process. At the same time, particles at such fine sizes can be more readily buoyed to the top of the flotation cell by air bubbles that adhere to them.

The flotation step is accomplished by the preparation of a pulp, consisting of a solid–liquid slurry that may contain up to 40% solids, to which chemical reagents known as collectors are added in a conditioning tank. The reagents are added to render some minerals hydrophobic so that they selectively adhere to air bubbles introduced into the pulp in a flotation cell. On the other hand, some reagents enhance selectivity through activation and depression phenomena. Frothers are also used to generate a mineral-laden froth layer and enhance particle–bubble adhesion. The products from the flotation cell are a concentrate and a tailings stream. The concentrate proceeds to the next step for further cleaning or treatment by hydro- or pyrometallurgical methods for the extraction of metals and other valuable compounds, while the tailings, which are ore components stripped of their valuable mineral content, are collected in lagoons known as tailings ponds. A typical froth flotation process can treat a ROM ore that assays 0.5% to a few percent copper to give

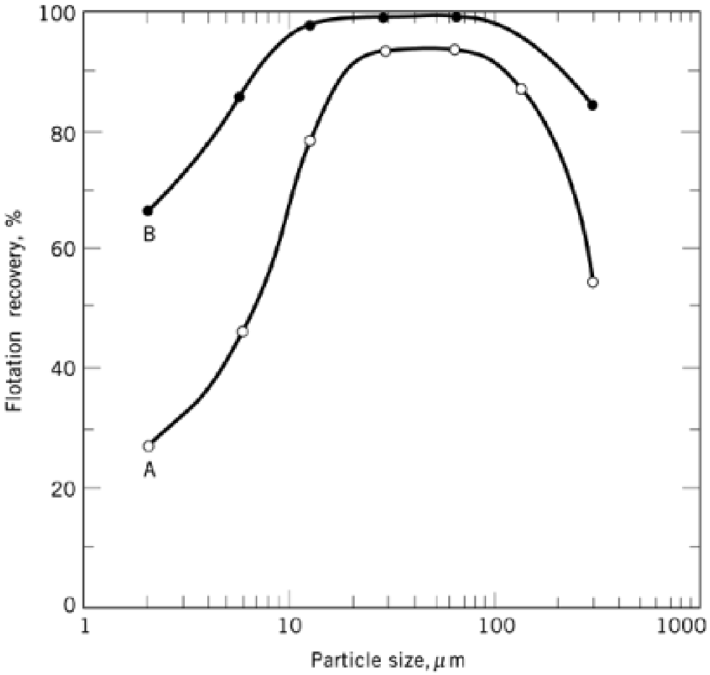


Fig. 1. Effect of particle size on the flotation recovery of a sulfide mineral. Mineral: chalcocite [2112-20-9], Cu_2S; reagent: potassium ethyl xanthate, C_2H_5OCSSK, 3.7 mg/L; flotation time: A, 0.5 min. and B, 2.0 min. Ref. 10.

a mineral concentrate analyzing 35% copper with a recovery of more than 85% of the copper content of the original ore.

The actual flotation phenomenon occurs in flotation cells usually arranged in batteries (12) and in industrial plants and individual cells can be any size from a few to 30 m^3 in volume. Column cells have become popular, particularly in the separation of very fine particles in the minerals industry and colloidal precipitates in environmental applications. Such cells can vary from 3 to 9 m in height and have circular or rectangular cross sections of 0.3 to 1.5 m wide. They essentially simulate a number of conventional cells stacked up on top of one another (Fig. 3). Microbubble flotation is a variant of column flotation, where gas bubbles are consistently in the range of 10–50 μm.

1.1. Process Design and Machinery

Following the field work of geologists and mining engineers and analyses (assays) to establish the grades (concentrations) of values in ores, a mineral concentration flow sheet is established on the basis of a number of preliminary tests. These include studies of comminution properties of the ore, liberation properties of the minerals, and optimization of conditions at which they occur. Reagent testing, choice of flotation conditions, pH, collectors, frothers, and auxiliary reagents follow. The locked cycle test is a design aid that allows the simulation of a full-scale flotation procedure prior to pilot-plant testing (13).

Flotation cells, also called flotation machines, exist in numerous designs differing in mode of agitation and method of gas introduction and dispersion. Flotation machine designs are largely empirical although once designed their specification and performance data can be expressed by mathematical relations (14). Figure 4 outlines one classification scheme of flotation machine types (15).

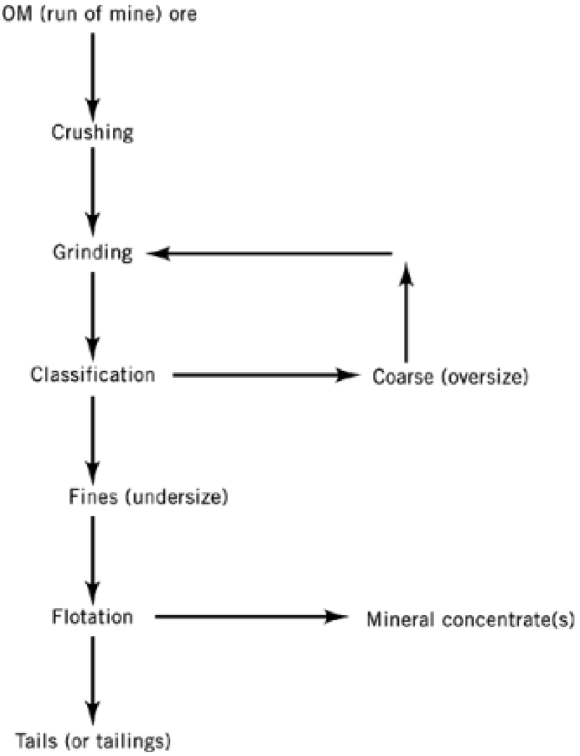


Fig. 2. A generic ore beneficiation flow sheet.

The processes that occur in a typical flotation cell are schematically shown in Figure 5 and consist of agitation, particle–bubble collision and attachment, flotation of particle–bubble aggregates, collection of aggregates in a froth layer at the top of the cell, removal of mineral-laden froth as concentrate, and flow of the nonfloating fraction as tailings slurry.

Figure 6 shows air dispersion and pulp agitation mechanisms in commercial open flow machines (16).

2. Interfacial Phenomena

Flotation is a surface chemistry-based process, where numerous phenomena that simultaneously occur at the solid–liquid–air interfacial region determine its outcome (17). In this context, the variable known as contact angle θ illustrated in Figure 7, is an important correlative parameter. At $\theta = 0^\circ$, the liquid spreads on the solid; in aqueous media in contact with air such a solid is said to be hydrophilic and is wetted by water. Air bubbles do not adhere to hydrophilic solids in water. Conversely, hydrophobic solids are not wetted by water; air bubbles do adhere to them and the value of the contact angle is larger than zero degrees, ie, $\theta > 0^\circ$.

The three interfacial tensions at equilibrium (Fig. 7) conform to Young's equation (eq. 1): where γ represents solid–gas, solid–liquid, and liquid–gas interfacial tension as indicated by subscripts.

$$\gamma_{\mathrm{sg}} - \gamma_{\mathrm{sl}} = \gamma_{\mathrm{lg}} \cos\theta \qquad (1)$$

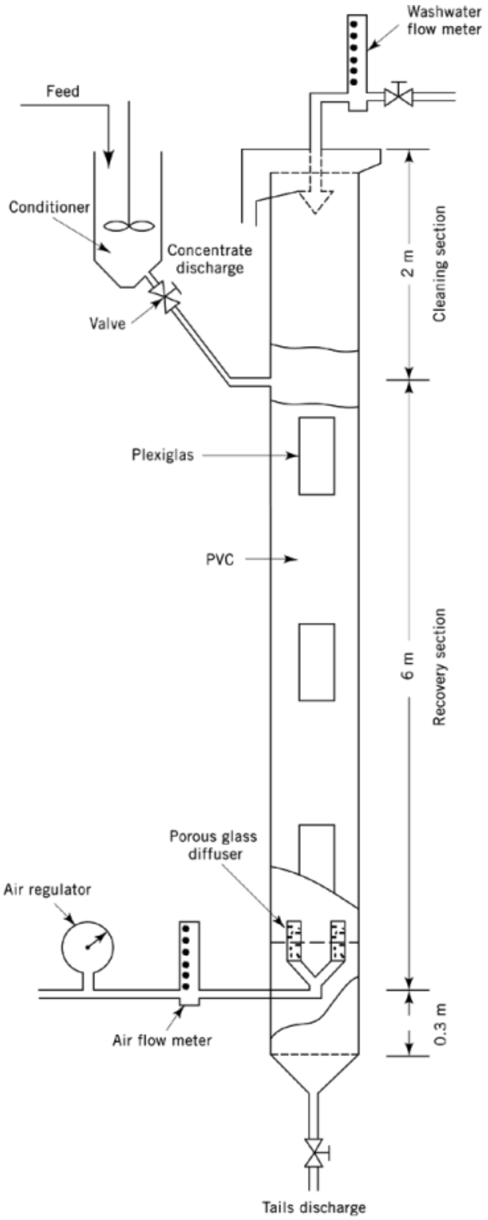


Fig. 3. A typical column flotation cell and peripherals.

Strictly speaking, equation 1 represents a special case that does not take into consideration the effects of gravity or external forces such as electric and magnetic fields (18). It also needs to be modified for rough (nonflat) and heterogenous (impure) surfaces as well as corner and edge effects. However, it has a thermodynamic basis and is widely utilized to account for wetting and spreading phenomena that occur between the three phases when they are in contact. Soldering, welding, joining, and detergency (qv), are but a few examples of systems besides

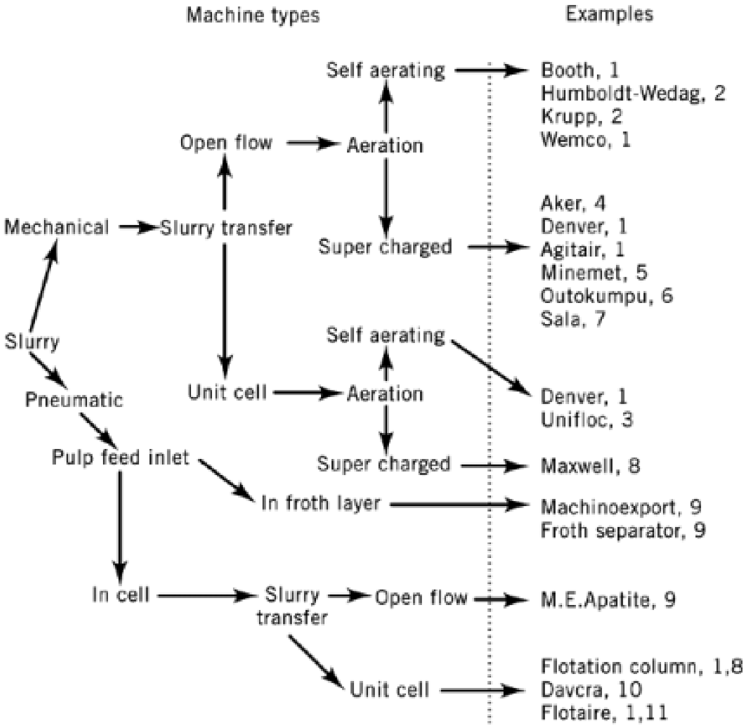


Fig. 4. Classification of flotation machine types and examples of brand names. Numbers indicate countries of origin of machines. 1, United States; 2, Germany; 3, United Kingdom; 4, Norway; 5, France; 6, Finland; 7, Sweden; 8, Canada; 9, former USSR; 10, Australia; and 11, South Africa. Ref. 15.

flotation where wetting and spreading phenomena play significant roles. Some contact angle values for solids in contact with aqueous media are given in Table 1.

2.1. Electrical Phenomena at the Solid–Liquid Interface

Solid particles, such as minerals, in contact with water, as in a flotation pulp, undergo an electrical charge rearrangement at the water–solid interface because of hydration and ion dissolution from the lattice, ion adsorption from the aqueous environment, as well as lattice defects and substitutions. Thus an electrical double layer surrounding the particles is established. The double layer can consist of wall charges, then a layer of chemically bonded ions followed by, moving further into the liquid, a layer that consists of compactly packed, solvated ions (Stern layer) after which the diffuse part of the double layer starts. In Figure 8, only the wall, the Stern layer, and diffuse part of the double layer are shown. Specific adsorptions occur within the first few atomic diameters (0.1–0.6 nm), whereas the diffuse part of the double layer can extend to tens of nanometers depending on the ionic strength (salt concentration) of the medium. According to the DLVO theory of colloid stability, the thickness of the double layer is highest at the lowest ionic strength (see Colloids).

The chemical composition, stoichiometry, and crystal structures of the solids in contact with water also play important roles in the degree of hydration that occurs at the solid–liquid interface and adsorption phenomena that affect the flotation process. The manner of cleavage or breakage of crystals is significant. A higher number of broken bonds at the cleavage (or breakage) surface indicates the possibility of a solid wall being more likely to take up water molecules.

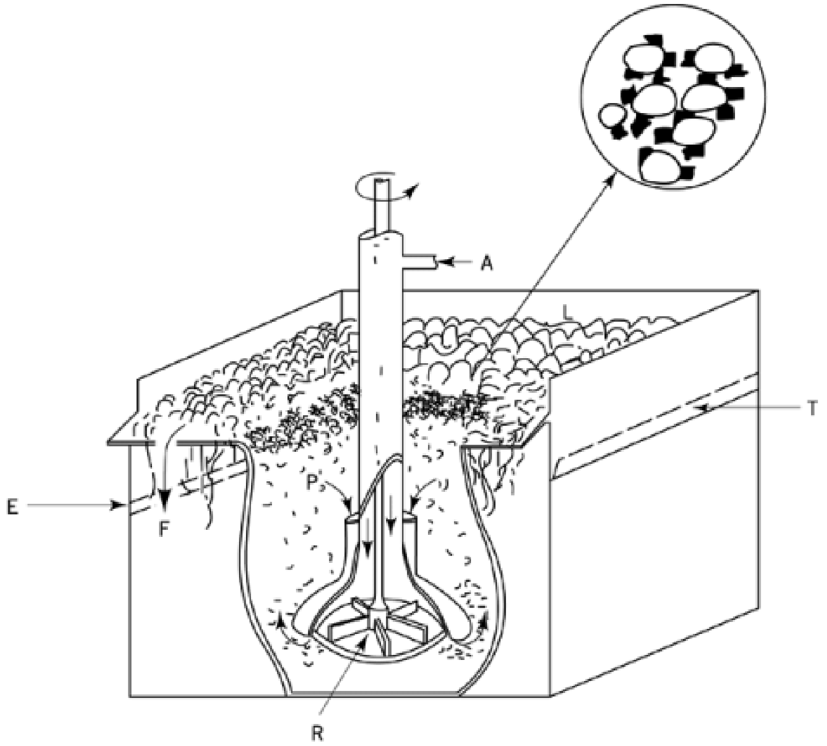


Fig. 5. Processes that occur in a flotation cell: A, air supply; E, slurry inlet; F, froth overflow; L, froth layer; inset, mineralized bubbles; P, flotation pulp; R, pulp agitation assembly (see Fig. 6); and T, tailings exit port.

The zeta potential (Fig. 8) is essentially the potential that can be measured at the surface of shear that forms if the solid was to be moved relative to the surrounding ionic medium. Techniques for the measurement of the zeta potentials of particles of various sizes are collectively known as electrokinetic potential measurement methods and include microelectrophoresis, streaming potential, sedimentation potential, and electroosmosis (19). A numerical value for zeta potential from microelectrophoresis can be obtained to a first approximation from equation 2, where η = viscosity of the liquid, ϵ = dielectric constant of the medium within the electrical double layer, V_e = electrophoretic velocity, and E = electric field $\cdot$

$$\zeta = (4\pi\eta/\epsilon)\ (V_e/E) \qquad (2)$$

The zeta potential and contact angle as well as flotation recovery correlate well in some flotation systems as shown in Figure 9 (20).

In principle, zeta potential allows the definition of an isoelectric point (IEP) for each mineral (or suspended solid) that defines the conditions at which the measured zeta potential is equal to zero. IEP is also known as point of zero charge (PZC) when the surface carries no net charge. This is the condition at which the net charge on the wall of the particle is electrostatically compensated by an equal and oppositely signed quantity of charge in the diffuse part of the electrical double layer. Most IEP values of solids are reported to reflect the pH at which this condition is satisfied. However, the condition of ($\zeta = 0$ V) can also be readily expressed in terms of the concentration of ions other than H^+. Examples of IEP values for some solids are tabulated in Table 2.

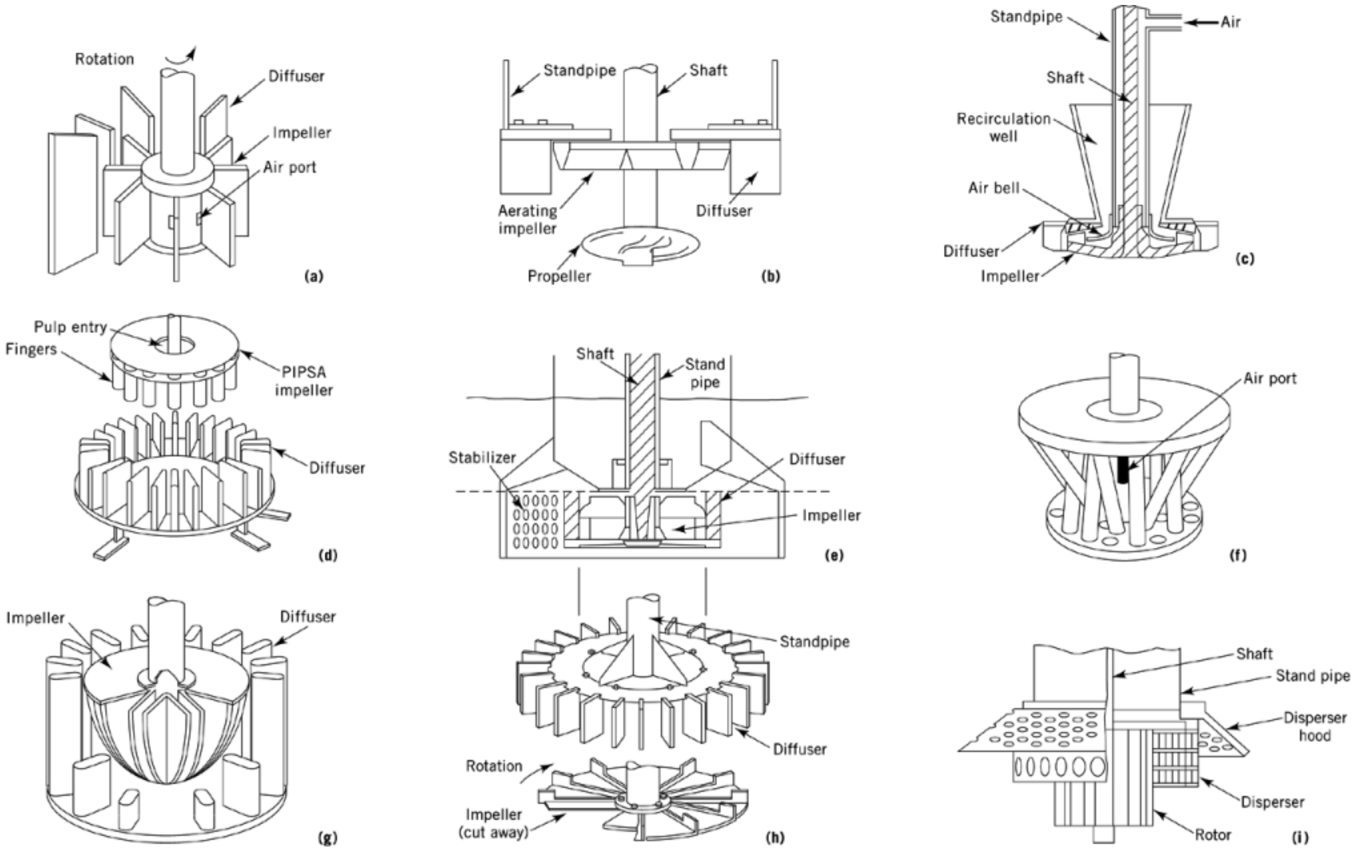


Fig. 6. Air dispersion and pulp agitation mechanisms in commercial flotation machines (16) (a) Aker (b)

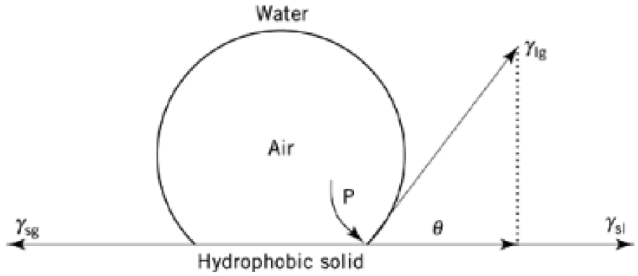


Fig. 7. The concept of contact angle with a captive bubble in an aqueous medium, adhering to a hydrophobic solid: P is the three-phase contact point. Here, the vector γ_{lg} passes through P and forms a tangent to the curved surface of the air bubble. The contact angle θ is drawn into the liquid.

Figure 10 shows the relationship between the IEP and the floatability of a typical oxide mineral (21). When pH < IEP and $\zeta > 0$ anion-type surfactants adsorb at the solid–liquid interface, whereas at pH > IEP and $\zeta < 0$, cation-type surfactants act as flotation collectors.

Table 1. Contact Angle Values for Solids in Contact with Aqueous Media

Solid	CAS Registry Number	Conditions	Contact angle, θ^a
colemanite	[12291-65-5]	5×10^{-3} *M* sodium oleate	43
copper (metal)	[7440-50-8]	1.5×10^{-4} *M* sodium oleate	93
fluorite	[7789-75-5]	10^{-5} *M* sodium oleate, pH = 8.1	91
galena	[12179-39-4]	10^{-3} *M* potassium ethyl xanthate	60
graphite	[7782-42-5]	water	86–96
ilmenite	[12168-52-4]	sodium oleate solution, $T = 75°C$, pH = 8	80
coal (high rank)		water	45–60
oil shale[b]		water	59.5
paraffin wax		water	108–111
silica	[7631-86-9]	1.1×10^{-5} *M* dodecylammonium chloride, pH = 10	81
stibnite	[1317-86-8]	water	84
Teflon	[9002-84-0]	water	160
Teflon		methanol in water solutions[c]	0

[a] Degrees.

[b] From Colorado, organic carbon = 28%.

[c] All concentrations with $\gamma_{\text{lv}} \leq 20$ mN/m(= dyn/cm).

Table 2. Isoelectric Points of Some Solids in Aqueous Media

Solid	pH[a]
AgCl	$pAg^+ = 4$
AgBr	$pAg^+ = 5.4$
Ag_2S	$pAg^+ = 10.2$
$CuSiO_3 \cdot 2\,H_2O$	$pCu^{2+} = 4$, at pH = 7
$CaCO_3$	5–12
CaF_2	$pCa^{2+} = 3$
Fe_2O_3	6.5 and 8.5
Fe_3O_4	6.5
FeS_2	7
$MgCO_3$	2–11.5
PbS	3.5
SiO_2	2–3.7
SiO_2	7[b]

[a] Unless otherwise noted. p indicates $-\log_{10}$ of concentration.

[b] In the presence of 3×10^{-3} *M* dodecylammonium acetate.

3. Chemicals in the Flotation Process

Flotation reagents are used in the froth flotation process to (*1*) enhance hydrophobicity, (*2*) control selectivity, (*3*) enhance recovery and grade, and (*4*) affect the velocity (kinetics) of the separation process. These chemicals are classified based on utilization: collector, frother, auxiliary reagent, or based on reagent chemistry: polar, nonpolar, and anionic, cationic, nonionic, and amphoteric. The active groups of the reagent molecules are typically carboxylates, xanthates, sulfates or sulfonates, and ammonium salts.

According to the first classification, collectors (also sometimes known as promoters) are the reagents that impart hydrophobicity to the solid to be floated (Table 3). Frothers lead to the creation of a froth layer at the top of the flotation cell and also enhance collector action by reducing the induction time, the time it takes for

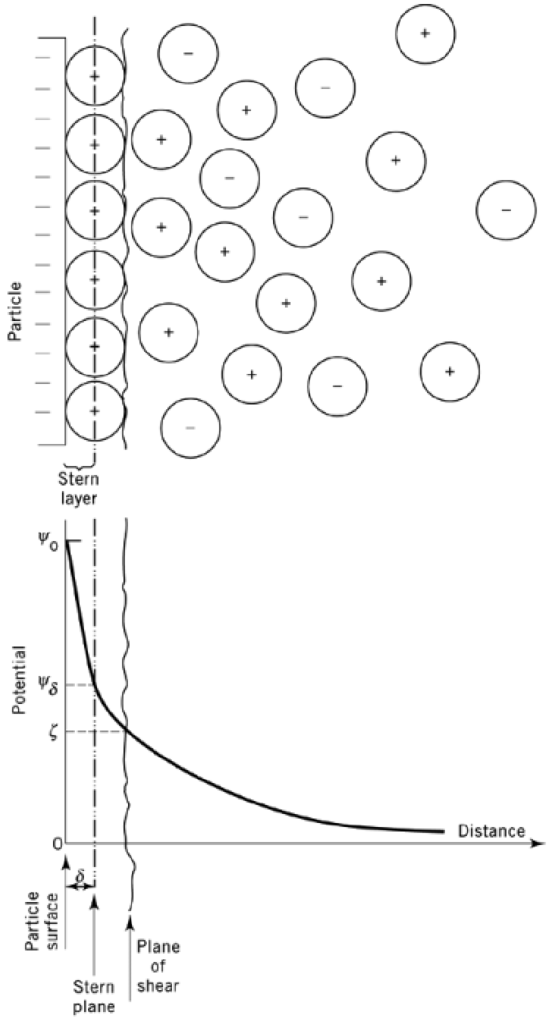


Fig. 8. Electrical double layer of a solid particle and placement of the plane of shear and zeta potential. ψ_o=Wall potential, ψ_δ=Stern potential (potential at the plane formed by joining the centers of ions of closest approach to the solid wall), ζ=zeta potential (potential at the shearing surface or plane when the particle and surrounding liquid move against one another). The particle and surrounding ionic medium satisfy the principle of electroneutrality.

air bubbles to adhere to the hydrophobic solid grains with which they collide (Table 4). Auxiliary reagents comprise pH regulators, oxidizing-reducing agents, and colloidal and polymeric additives (Tables 5 and 6). The flotation of naturally hydrophobic solids using chemicals, not conventionally known as flotation collectors, is called collectorless flotation.

An inherent drawback of classifying flotation reagents according to their function in the flotation process is that what acts as a frother in one flotation system might play both collecting and frothing roles in another. For example, long-chain alcohols (see Table 4) are recognized as frothers in most flotation systems, but they act both as collectors and frothers in coal, talc, or graphite-containing flotation pulps.

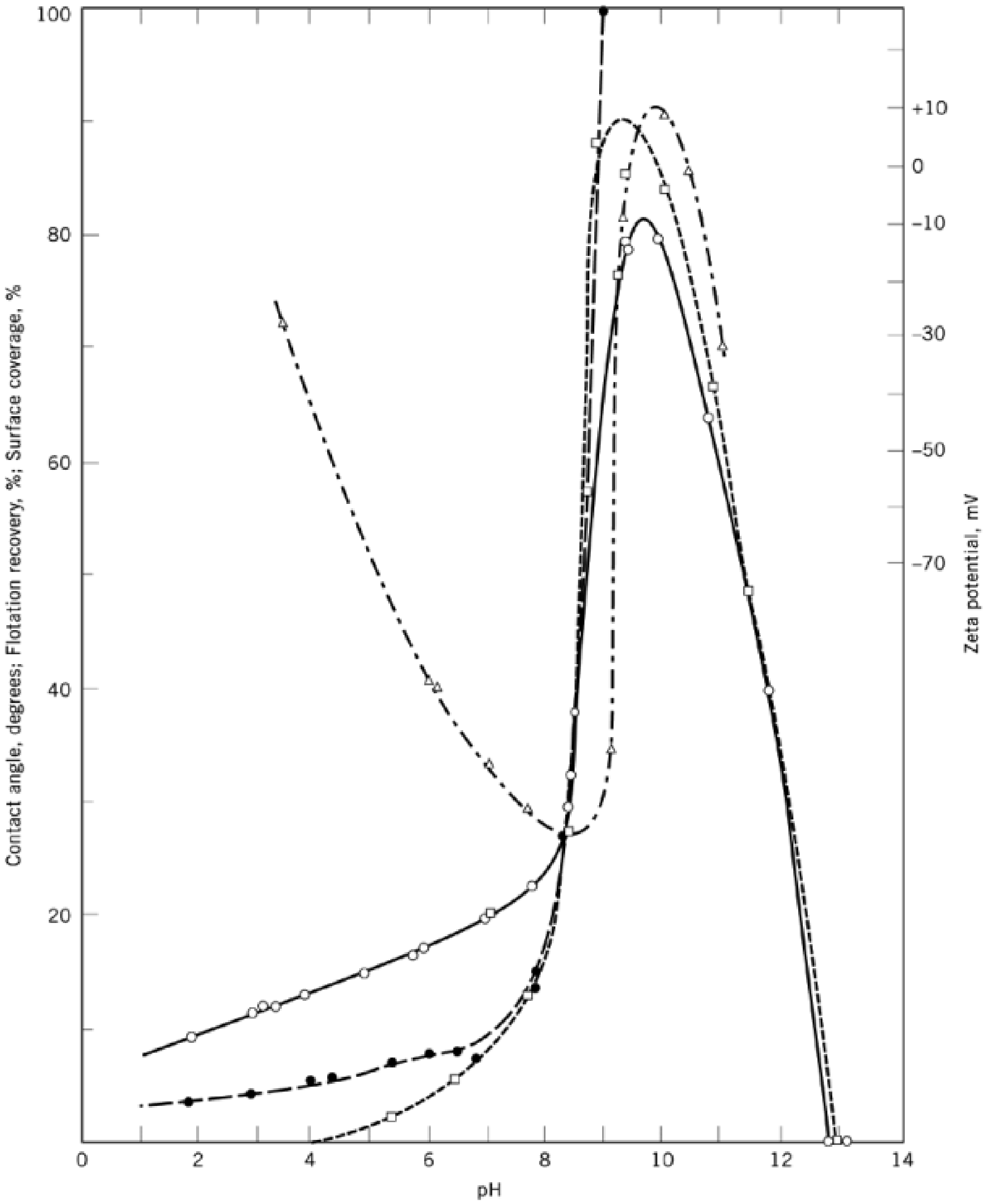


Fig. 9. Correlation of contact angle, flotation recovery, surface coverage by collector, and zeta potential. Solid, quartz, collector reagent, $4\times10^{-4}\ M$ dodecylammonium acetate. □=recovery, %; △=zeta potential, mV; ○=contact angle, degrees; and ●=surface coverage, % of one monolayer. Ref. 20.

3.1. Interaction of Solids With Flotation Reagents

For flotation to occur with the aid of reagents, such compounds must adsorb at the solid–liquid interface unless the solid to be floated is naturally hydrophobic. In this latter case only depression can be attempted by the use of additional ions or depressants that hinder bubble–particle adhesion. Frothers (typically long-chain alcohols)

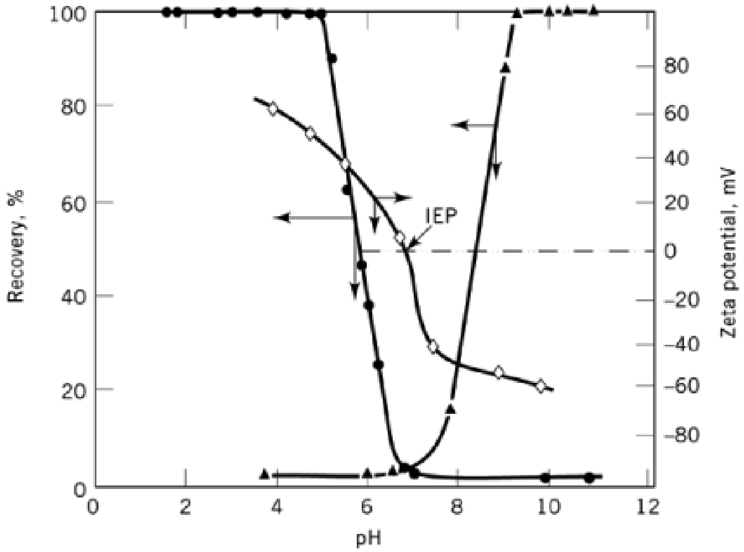


Fig. 10. Relationship between the IEP and the floatability of a typical oxide mineral (Goethite: $Fe_2O_3 \cdot H_2O$). At $pH > pH_{IEP}$ the zeta potential has a negative sign and the collector is cationic, whereas at $pH < pH_{IEP}$ the zeta potential carries a positive sign and the effective collector is anionic. ●, recovery with sodium dodecyl sulfate or sodium dodecyl sulfonate; ▲, recovery with dodecyl ammonium chloride; and ◇, zeta potential.

and/or modifying agents such as hydrocarbon oils can, however, be used to enhance the collection of naturally hydrophobic solids such as MoS_2, talc, or plastics.

Table 3. Flotation Collectors Used in the Minerals Industry and Their Areas of Application

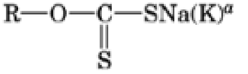
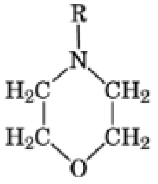
Compound	Active ingredient	Common application
alkyl thiocarbonates (xanthates)	 $R{-}O{-}\underset{\underset{S}{\|}}{C}{-}SNa(K)^{a}$	sulfides, metallic minerals
	a	
alkyl morpholines		potash
alkyl sulfonates	$R{-}SO_3^-M^+$	carbonates, hematite, borates, magnetite
alkyl sulfates	$R{-}O{-}SO_3^-M^+$	similar to sulfonates

Table 3. ***Continued***

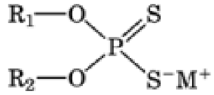
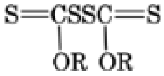
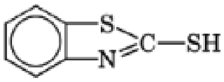
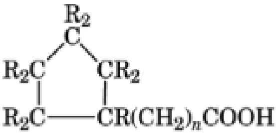
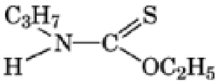
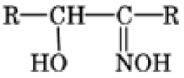
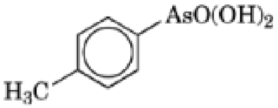
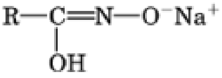
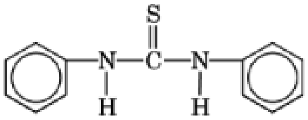
Compound	Active ingredient	Common application
dialkyl dithiophosphates (aerofloats)		native gold, copper, and sulfides
dixanthogens	 $S{=}\underset{OR}{C}SS\underset{OR}{C}{=}S$	sulfides
hydrocarbon oils[b]	C_nH_{2n+2}	coal, molybdenite, borates
mercaptobenzothiazole		pyrite
naphthenic acids		fluorite, borates
O-ethyl isopropyl-thiocarbamate		copper sulfides
oximes	 $R{-}\underset{HO}{CH}{-}\underset{NOH}{\overset{\|}{C}}{-}R$	chrysocolla, cassiterite
p-tolyl arsonic acid		cassiterite
primary amine salts	$RNH_3^+Cl^-$	silica, silicates, sylvite
quaternary ammonium salts	$RN(CH_3)_3^+Cl^-$, $R = C_{10} - C_{16}$	silica, silicates, oxides
sodium alkyl hydroxamates	 $R{-}\underset{OH}{C}{=}N{-}O^-Na^+$	wolframite, cassiterite, hematite

Table 3. ***Continued***

Compound	Active ingredient	Common application
sodium carboxylates	$RCOO^-Na^+$	carbonates, phosphate rock, fluorite, hematite
thiocarbanilide[c]		sulfides
xanthogen formates (minerec)	 $R{-}O{-}\overset{S}{\overset{\Vert}{C}}{-}S{-}\overset{S}{\overset{\Vert}{C}}{-}OR$	sulfides

[a] R is an alkyl group with one to five carbons.

[b] Eg, vapor oil, kerosene, fuel oils.

[c] *N,N*-Diphenylthiourea [102-08-9].

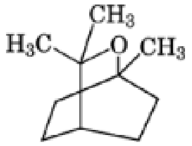
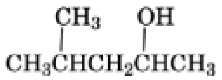
3.1.1. Adsorption Mechanisms

The following mechanisms of adsorption are responsible for the formation of mineral–reagent bonds.

3.1.2. Electrostatic Interactions

This is the mechanism that operates when adsorption sites and reagents carry opposite electrical charge signs.

Table 4. Examples of Flotation Frothers Widely Utilized in the Minerals Industry

Common name and composition	Chemical structure of active component
aliphatic alcohols (long-chain)	$CH_3{-}(CH_2)_n{-}CH_2OH$
eucalyptus oil[a]	
methylisobutyl carbinol[b] MIBC	 $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2\overset{OH}{\overset{\vert}{C}}HCH_3$
pine oil	mixture of terpineols
poly(propylene glycol) monoalkyl ethers[c]	$R(OC_3H_6)_nOH$ $n = 2 - 5$, $R = CH_3$, C_4H_9
poly(ethylene glycol)s	$R(OC_2H_4)_nOC_2H_4OH$ $n = 2 - 5$

[a] Cineole or eucalyptol [470-82-6] is the principal component.

[b] 4-Methyl-2-pentanol [108-11-2].

[c] Trade name = Dowfroth−250.

Table 5. Inorganic Chemicals Used as Auxiliary Reagents

Name	CAS Registry Number	Composition	Area of use
cupric sulfate	[7758-98-7]	$CuSO_4$	sphalerite and arsenopyrite activator
lead acetate	[301-04-2]	$Pb(CH_3COO)_2$	stibnite activator
lime	[1305-78-8]	CaO	pH regulator, depressant, activator
Nokes reagent		complex mixture[a]	selective depressant in molybdenite circuits; improves molybdenite grade
sodium silicate	[1344-09-8]	Na_2SiO_3	dispersant–depressant for siliceous gangue, clays
sodium dichromate	[10588-01-9]	$Na_2Cr_2O_7$	galena depressant
sodium cyanide	[143-33-9]	NaCN	metal sulfide depressant
sodium hydroxide	[1310-73-2]	NaOH	pH regulator, dispersant
sodium sulfide	[1313-82-2]	Na_2S	sulfide depressant, sulfidizer
sodium carbonate	[497-19-8]	Na_2CO_3	pH regulator, dispersant
sulfur dioxide	[7446-09-5]	SO_2	depressant for sphalerite
sulfuric acid	[7664-93-9]	H_2SO_4	pH regulator

[a] Includes P_2S_5, As_2O_3, Sb_2O_3, and NaOH.

3.1.3. Hydrogen Bond Formation

This facilitates adsorption if the mineral and the adsorbate have any of the highly electronegative elements S,O,N,F, and hydrogen. A weak (physical) bond is established between the solid wall and the reagent through the alignment of the cited elements.

3.1.4. Collectors Fitting into Lattice Cavities

Lattice site fitting of collectors at solid walls has been invoked as a means of explaining the selective behavior of amines (cationic collectors) as reagents in the flotation-separation of soluble salt minerals such as KCl and NaCl (22).

3.1.5. Chemical Bond Formation (Chemisorption)

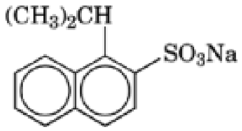
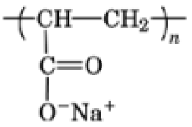
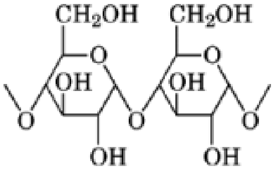
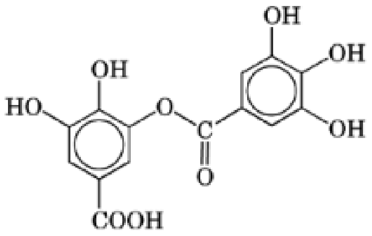
This is the mechanism that leads to the formation of the strongest bonds between collectors and mineral surfaces. Chemically adsorbed reagents usually form surface compounds at the active wall sites. The flotation of calcite ($CaCO_3$) and apatite ($Ca_3(PO_4)_2$) by fatty acids such as oleic acid ($C_{17}H_{35}COOH$) is a typical example of where strong mineral–collector bonds of this nature form.

3.1.6. Crystal Field Adsorption and Hydrophobic Bonding

These are two other mechanisms that operate in reagent adsorption processes (23, 24). The former has been suggested to explain the adsorption of polyacrylamide (a potential flotation depressant) onto fluorite (CaF_2) and the latter is a mechanism that is more frequently invoked where the hydrocarbon ends of surfactant molecules used as flotation reagents aggregate to form micelles in the solution or hemimicelles near the wall of the solid (25). The hydrocarbon ends of amphipatic molecules (surfactants) adsorb onto hydrophobic surfaces by the same mechanism. The action of vapor oil in molybdenite (MoS_2) flotation and the use of Vaseline-type collectors in the grease table collection of diamonds are further examples of systems where hydrophobic bonding can be suggested as the operational bonding mechanism.

Electrochemical processes at some sulfide mineral surfaces lead to the formation of oxidation products as in the case of the hydrophobization of galena (PbS) by xanthates ($ROCSS^-$) or the oxidation of pyrite (FeS_2) or chalcopyrite ($CuFeS_2$) surfaces, which generate hydrophobic layers. Arguably these represent mechanisms of mineral surface hydrophobization and not necessarily flotation reagent adsorption mechanisms.

Table 6. Organic Auxiliary Reagents Used in Froth Flotation Technology

Name	Active component	Area of application
poly(ethylene oxide) [25322-68-3]	$-(CH_2-CH_2-O)_n-$	flocculant, filtration aid
quebracho[a]	mixture of polyhydroxy-cyclic carboxylic acids and other cyclic components	carbonate and fluorite depressant, defoaming agent
sodium isopropyl naphthalene sulfonate[b] [28348-64-3]		wetting agent, defoaming agent, emulsifier
sodium dioctyl-sulfosuccinate[c]	 $NaO_3SCH(CH_2COOC_8H_{17})COOC_8H_{17}$	similar to aerosol OS
sodium polyacrylate	 $-(CH(C(=O)O^-Na^+)-CH_2)_n-$	flocculant, thickening and filtration aid
starch [9005-25-8]		slime depressant, hematite depressant
tannic acid [1401-55-4]		fluorite and carbonate depressant, defoamer

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[a] Shinopsis tree extract.
[b] Aerosol OS.
[c] Aerosol OT.

3.1.7. Other Interaction Processes

The selectivity of flotation reagents in a pulp and their functions depend on their interactions with the mineral phases to be separated, but other physicochemical and hydrodynamic processes also play roles. All adsorption–desorption phenomena occur at the solid–liquid interfacial region. Surface processes that influence such adsorptions include activation and depression. Activators and depressants are auxiliary reagents.

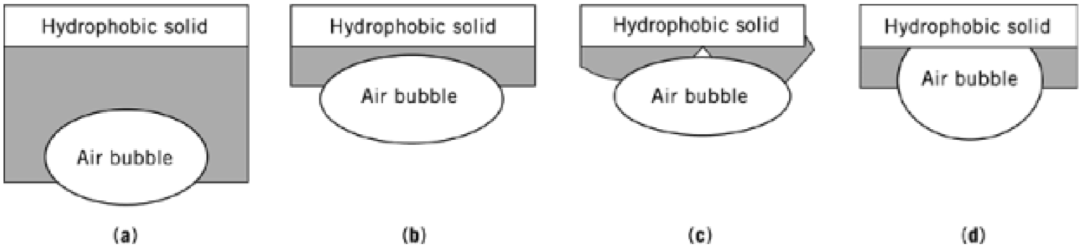

Fig. 11. Stages of disjoining film behavior in flotation upon particle–bubble collision: (**a,b**) film thinning; (**c**) film rupture; and (**d**) film recession and particle–bubble adhesion.

Activators enhance the adsorption of collectors, eg, Ca^{2+} in the fatty acid flotation of silicates at high pH or Cu^{2+} in the flotation of sphalerite, ZnS, by sulfohydryl collectors. Depressants, on the other hand, have the opposite effect; they hinder the flotation of certain minerals, thus improving selectivity. For example, high pH as well as high sulfide ion concentrations can hinder the flotation of sulfide minerals such as galena (PbS) in the presence of xanthates ($ROCSS^-$). Hence, for a given fixed collector concentration there is a fixed critical pH that defines the transition between flotation and no flotation. This is the basis of the Barsky relationship which can be expressed as $[X^-]/[OH^-]$ = constant, where $[X^-]$ is the xanthate ion concentration in the pulp and $[OH^-]$ is the hydroxyl ion concentration indicated by the pH. Similar relationships can be written for sulfide ion, cyanide, or thiocyanate, which act as typical depressants in sulfide flotation systems.

4. Flotation Kinetics

It is possible to analyze froth flotation as a probability process, ie,

$$P_f = P_c \cdot P_a P_s \qquad (3)$$

where P_f, P_c, P_a, and P_s are probability of flotation, particle–bubble collision, particle–bubble adhesion, and formation of a stable particle–bubble aggregate, respectively. Numerous variables affect these probability functions, eg: (*1*) particle and bubble sizes, pulp density, and number of bubbles in the pulp, as well as the intensity of agitation are primary variables that affect the probability of particle–bubble collisions; (*2*) the probability of particle–bubble adhesion, that is, the formation of particle–bubble bond(s) depends on the value of the contact angle, directional angle of impact and velocity of collision, the presence of frother in the medium and the resistance of the disjoining film at the interface; (*3*) the probability of formation of particle–bubble aggregates that can sustain the particle–bubble bond depends on the strength of this bond at the hydrodynamic conditions which prevail in the agitated flotation pulp.

Disjoining pressure measures the strength of the liquid film between the bubble and the particle when the two collide (26). Thus a hydrophilic solid has a film that exhibits a high disjoining pressure whereas the disjoining pressure on a hydrophobic solid is very small. When a particle and bubble collide the disjoining film deforms, thins, ruptures, and recedes, upon which particle–bubble attachment is completed as illustrated in Figure 11. The time it takes for this process to occur is known as induction time and varies from 10 ms to one millisecond.

Flotation process kinetics determine the residence time, the average time a given particle stays in the flotation pulp from the instant it enters the cell until it exits. One way to study flotation kinetics is to record flotation recoveries as a function of time under a given set of conditions such as pulp pH, collector concentration, particle size, etc. The data allow the derivation of an expression that describes the rate of the process.

$$(dC/dt) = -kC^n \qquad (4)$$

where C = concentration of solids left in the flotation cell, t = time, k = rate constant, and n = order of the process.

First-order kinetics (ie, $n = 1$) is frequently assumed and seems adequate to describe the kinetics of most flotation processes. However, highly hydrophobic particles float faster and very fine particles or coarse ones outside the optimal flotation size range (see Fig. 1) take longer to collect in the froth layer. Excellent reviews of the subject are available in the literature (27).

Two technologically significant concepts in mineral concentration processes including froth flotation are recovery and grade. Recovery quantifies the percentage of value mineral collected in the froth layer whereas grade represents the chemical analyses of starting materials and products. The grade of an ore or a concentrate with respect to a valuable component indicates the percentage of this component in it. For example, a copper ore concentrate that assays 35% Cu has a grade of 35% Cu. Similarly, recovery indicates the percentage of total valuable material initially available in the feed which ends up in the concentrate fraction. Thus 80% recovery of copper indicates that 80% of the copper in the ore fed to the flotation circuit has been recovered in the concentrate, the remaining 20% having been lost into the tailings stream. Recovery and grade tend to vary inversely to one another.

5. Applications

5.1. Sulfide Ore Flotation.

Sulfide minerals, frequently cited as metallic minerals, occur mostly in complex ore bodies that bear a multitude of sulfides together with gangue. Thus it is quite common to find a complex sulfide ore body that contains galena [12179-39-4], PbS; sphalerite [12169-28-7], ZnS; chalopyrite [1308-56-1], $CuFeS_2$; and pyrite [1309-36-0], FeS_2, as primary sulfide minerals, and gangue usually as silica (SiO_2), silicates, or carbonate minerals. The treatment of such an ore aims at the recovery of individual concentrates of lead, zinc, and copper-bearing minerals plus a pyrite concentrate whereas gangue minerals end up in the tailings stream. Figure 12, for example, is a flow sheet suggested after a laboratory study of an ore that contains copper and zinc as the valuable minerals.

A number of generalizations can be made regarding the use of froth flotation technology in sulfide mineral concentrations: (*1*) xanthates and dithiophosphates are suitable sulfide mineral flotation collectors; (*2*) the action of xanthates in sulfide mineral systems require the presence of oxygen, from air, for flotation to occur; (*3*) longer chain homologues of a straight-chain collector series are more effective collectors per unit weight. This is also true for collector systems other than xanthates; (*4*) auxiliary reagents, as with nonsulfide systems, can be used to enhance selectivity.

5.2. Nonsulfide Ore Flotation

Nonsulfide minerals recovered by flotation include native elements such as graphite, diamonds, copper, gold, and numerous oxides as well as salts such as carbonates, phosphates, tungstates, and the like. Examples of value-bearing nonsulfide, noncoal minerals include

apatite [1306-05-4] $Ca_3(PO_4)_2$
calcite [471-34-1] $CaCO_3$
cassiterite [1317-45-9] SnO_2
chrysocolla $CuSiO_3{\cdot}nH_2O$ [26318-99-0]
colemanite [12291-65-5] $Ca_2B_4O_{11}{\cdot}5H_2O$
hematite [1309-37-1] Fe_2O_3
ilmenite [12168-52-4] $FeO{\cdot}TiO_2$
kaolinite [1318-74-7] $Al_4Si_4O_{10}(OH)_8$

magnesite [13717-00-5] $MgCO_3$
rutile [13463-67-7] TiO_2
scheelite [14913-80-5] $CaWO_4$
silica [7631-86-9] SiO_2
smithsonite [14476-25-6] $ZnCO_3$

The basic flow sheet for the flotation-concentration of nonsulfide minerals is essentially the same as that for treating sulfides but the family of reagents used is different. The reagents utilized for nonsulfide mineral concentrations by flotation are usually fatty acids or their salts (RCOOH, RCOOM), sulfonates (RSO_3M), sulfates (RSO_4M), where M is usually Na or K, and R represents a linear, branched, or cyclic hydrocarbon chain; and amines $[R_1N(R)_3]A$ where R and R_1 are hydrocarbon chains and A is an anion such as Cl^- or Br^-. Collectors for most nonsulfides can be selected on the basis of their isoelectric points. Thus at $pH > pH_{IEP}$ cationic surfactants are suitable collectors whereas at lower pH values anion-type collectors are selected as illustrated in Figure 10 (28). Figure 13 shows an iron ore flotation flow sheet as a representative of high volume oxide flotation practice.

5.3. Soluble Salt Flotation.

KCl separation from NaCl and media containing other soluble salts such as $MgCl_2$ (eg, The Dead Sea works in Israel and Jordan) or insoluble materials such as clays is accomplished by the flotation of crystals using amines as collectors. The mechanism of adsorption of amines on soluble salts such as KCl has been shown to be due to the matching of collector ion size and lattice vacancies (in KCl flotation) as well as surface charges carried by the solids floated (22). Although cation-type collectors (eg, amines) are commonly used, the utility of sulfonates and carboxylates has also been demonstrated in laboratory experiments.

5.4. Coal Flotation.

Coal is a conglomerate of minerals, some of which are combustible. The primary objective of coal processing practice is to remove two types of components from the ROM ore: noncombustibles which are the ash-forming materials and sulfur-bearing compounds. The ash-forming components are shale, clays, calcite, and a small quantity of oxides such as SiO_2 or Fe_2O_3; the sulfur-bearing components are mostly pyrite (FeS_2). Sulfurous minerals are responsible for SO_x emissions during combustion. There is also a sulfur-bearing component in most coals which is not removable by physical means such as flotation. Methods for the elimination of this small percentage component known as structurally bound sulfur are available in the literature (29).

The reagents used in coal flotation are either those that collect coal, leaving the ash-forming compounds in the tailing, or those that float pyrite leaving a low sulfur coal concentrate. For coal flotation, nonionic reagents such as long-chain alcohols alone or together with nonpolar hydrocarbon liquids such as kerosene or fuel oil are commonly used. For pyrite flotation xanthates are widely applied whereas for shales and oxides cationic collectors such as amines together with a frother such as a long-chain alcohol or pine oil are used. A coal flotation flow sheet is given in Figure 14.

5.5. Water Treatment

Flotation in water treatment is used both for the removal of dissolved ions such as Cu^{2+}, Cr^{3+}, or $(PO_4)^{3-}$ or surfactants and suspended solids as in the case of sludge treatment. The final product in this case is purified

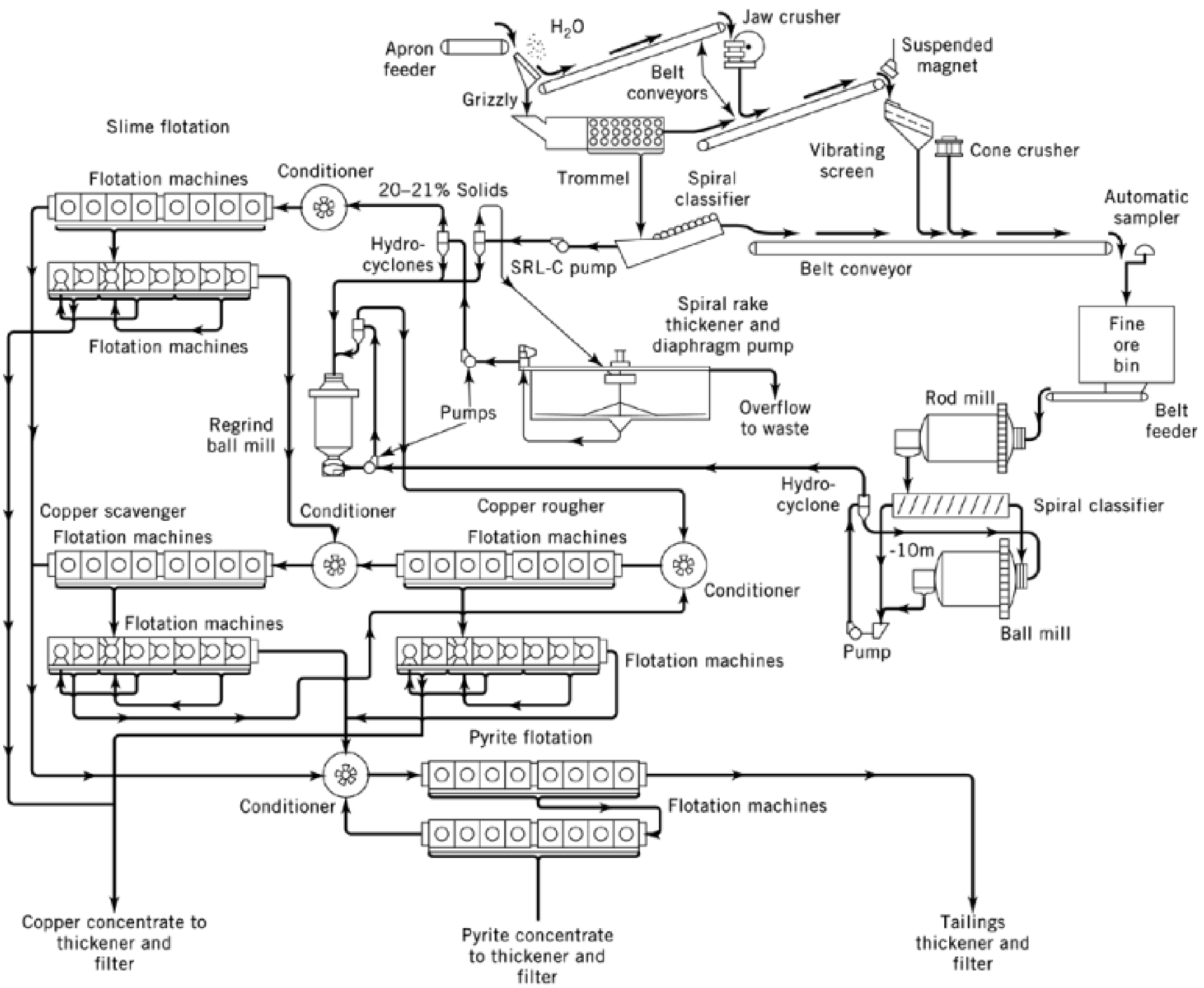

Fig. 12. Complex copper ore concentration flow sheet. Courtesy of Denver Equipment Co.

water rather than a mineral concentrate. Furthermore, water is treated either for drinking purposes (potable water preparation) or safe disposal to the environment.

In the removal of contaminating ions such as $(PO_4)^{3-}$; or Fe^{2+} a precipitate such as $Ca_3(PO_4)_2$ or $Fe(OH)_3$, after oxidizing ferrous ion to ferric, is formed and the solid is removed. The addition of surfactants is usually not essential (nor desirable) since most waters contain natural surfactants that would render the solids sufficiently hydrophobic for flotation to occur. Such surfactants derive from the degradation of organic matter, and humic substances abundantly available in nature (30).

Two main operational variables that differentiate the flotation of finely dispersed colloids and precipitates in water treatment from the flotation of minerals is the need for quiescent pulp conditions (low turbulence) and the need for very fine bubble sizes in the former. This is accomplished by the use of electroflotation and

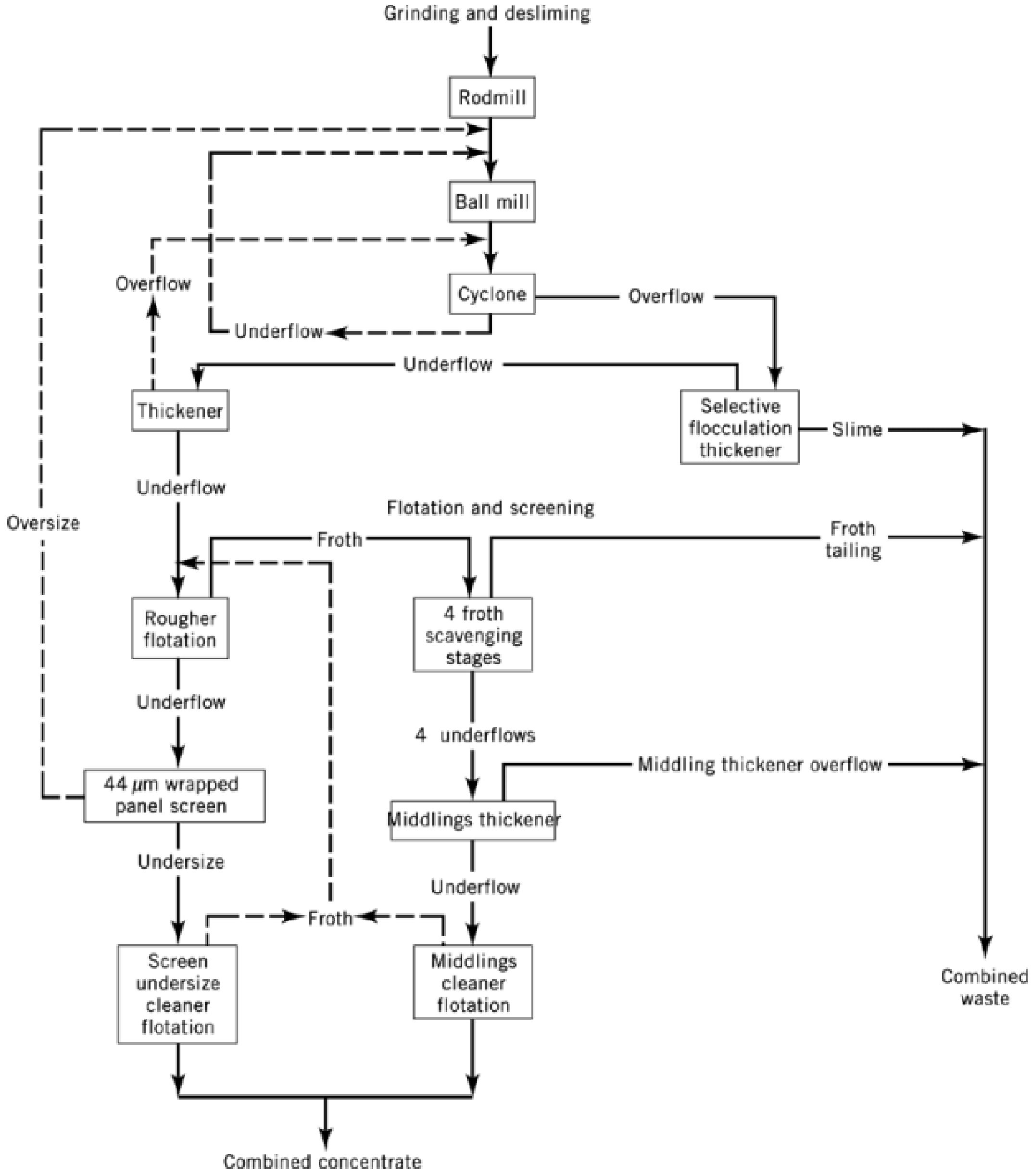

Fig. 13. Experimental iron ore flotation flow sheet (28): (__), forward flow; (_), return flow. Courtesy of USBM. Note the combination of flotation and flocculation in the same process. A plant based on this type of study has been built at the Tilden Mine (Michigan).

dissolved air flotation instead of mechanically generated bubbles which is common in mineral flotation practice. Electroflotation is a technique where fine gas bubbles (hydrogen and oxygen) are generated in the pulp by the application of electricity to electrodes. These very fine bubbles are more suited to the flotation of very fine particles encountered in water treatment. Its industrial usage is not widespread. Dissolved air flotation is

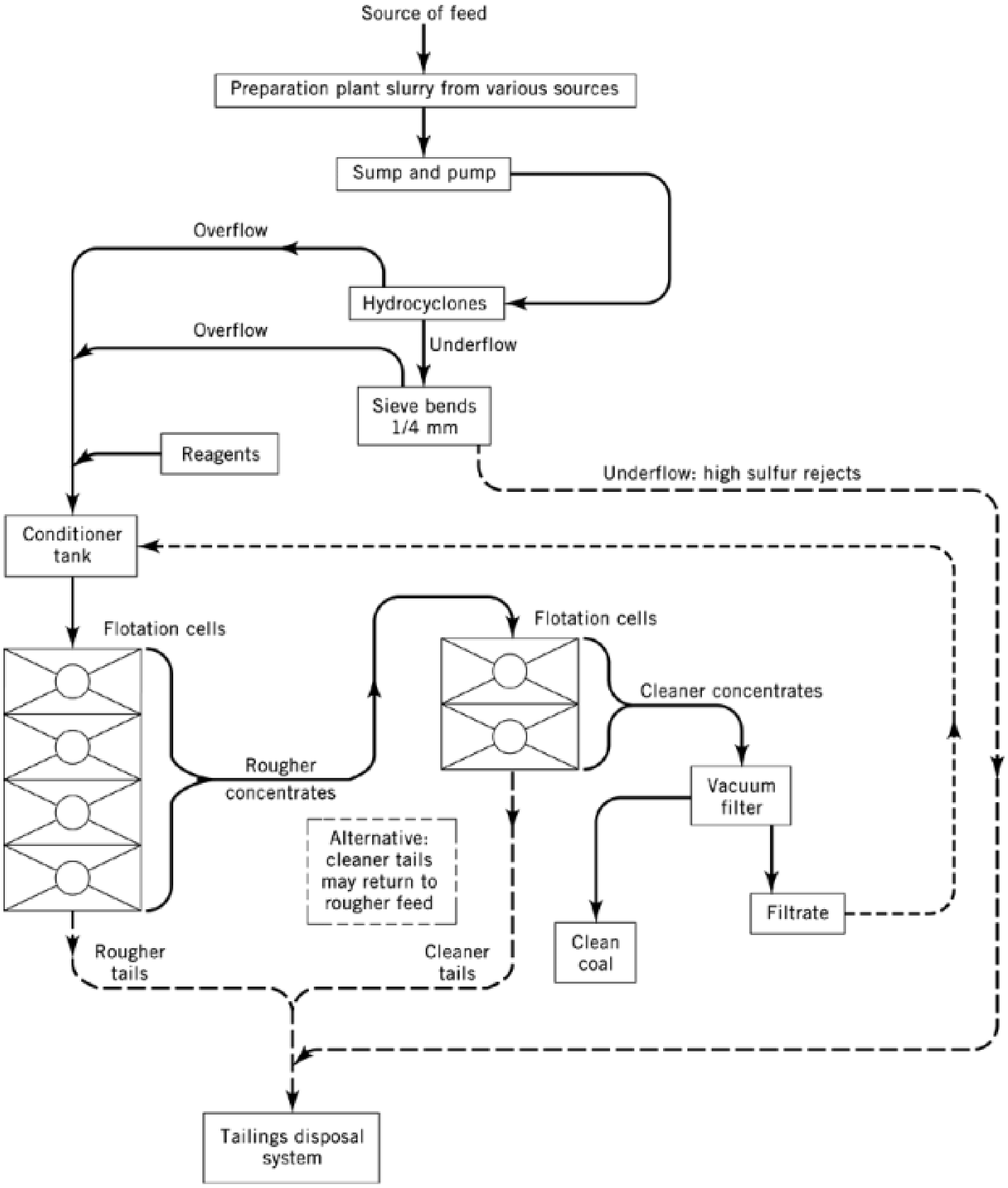

Fig. 14. Coal flotation flow sheet suggested for increased sulfur removal (29). Pyritic sulfur removal from coal makes it imperative to closely control pulp densities and reagent regimes.

similar to vacuum flotation. Air-saturated slurries are subjected to vacuum for the generation of bubbles. The process finds limited application in water treatment and in paper pulp effluent purification. The need to run it batchwise renders it less versatile.

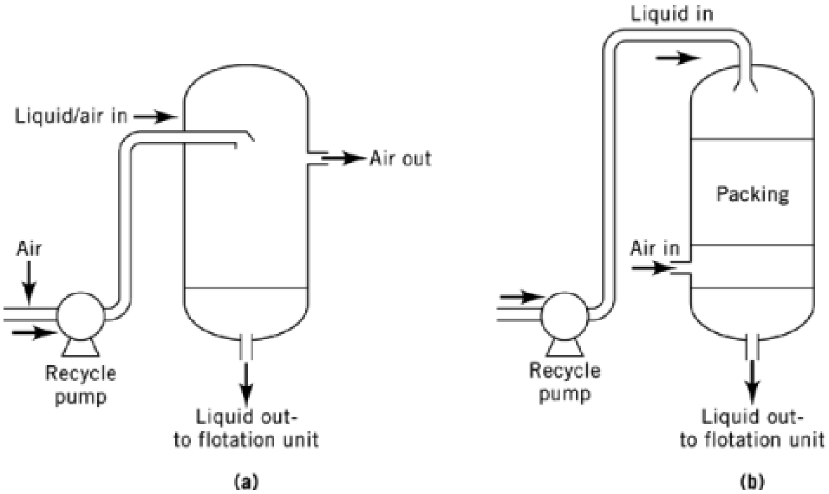

Fig. 15. Air-saturator systems used in the practice of water treatment by flotation (31). (**a**), Injection of air into suction line of recycle pump; (**b**), packed saturator.

Two air-saturation systems suited for use in water treatment are shown in Figure 15 (31). Such mechanisms facilitate the release of air that generates much finer bubbles than mechanical air dispersion methods used in mineral flotation practice.

5.6. Ion Flotation and Foam Separation.

Ions and dissolved surfactant molecules can be removed from solutions by the agency of foam. In this case ions are sandwiched in foam films. The scientific basis of these processes is well understood and successes of metal ion recovery from solutions including U, Pt, Au, as well as different surfactants (detergents) have been reported in the literature.

5.7. Gamma Flotation Process.

From consideration of the variables that influence the value of the contact angle on hydrophobic solids and Young's equation it can be seen that it should be possible to obtain $\theta = 0^\circ$ by manipulation of the surface tension of the liquid. Thus a plot of cos θ against γ_{lg} gives a straight line that extrapolates to $\cos\theta = 1$, $(\theta = 0^\circ)$ which allows the definition of a critical surface tension of wetting (γ_{c}). The critical surface tension of wetting of a solid can also be determined using flotation instead of contact angle measurements.

The concept of critical surface tension of wetting has been introduced (32) in connection with wetting phenomena in general and its application to froth flotation demonstrated (33, 34) using artificial mixtures of hydrophobic materials. The term gamma flotation has been coined to describe the use of surface tension control as a means of achieving selective flotation (35). The gamma flotation process relies on the exploitation of differences between the critical surface tension of wetting values of two hydrophobic solids in the same flotation pulp. By arranging the surface tension of the solution (pulp) to a value between the (γ_c) values of solids 1 and 2, solid 1 should float whereas solid 2 should remain hydrophilic and not adhere to air bubbles. The thermodynamical validity (36) of this approach and its applicability in flotation–separation has been demonstrated for various minerals (33, 34, 36–39). It has also been recognized that the process called salt flotation can be explained using the principles of gamma flotation (35).

5.8. Two-Liquid Flotation

There are certain advantages to the substitution of oil droplets for air bubbles in a flotation pulp. Among these is the fact that oil droplets can be produced at much finer sizes than mechanically dispersed air bubbles and thus finer particles collected. Attractive forces operating among molecules in air bubbles and in saturated hydrocarbon oils are mainly van der Waals forces which lead to hydrophobic bonding. The three-phase contact among oil, water, and solid can be represented as in Figure 7 with oil replacing air so that $\gamma_{\mathrm{gl}} = \gamma_{\mathrm{ow}}$, $\gamma_{\mathrm{sg}} = \gamma_{\mathrm{so}}$, and $\gamma_{\mathrm{sl}} = \gamma_{\mathrm{sw}}$. The spreading coefficients for oil on solid in the presence of water ($S_{\mathrm{o(w/s)}}$) and water on solid in the presence of oil ($S_{\mathrm{w(o/s)}}$) correlate as follows:

$$S_{\mathrm{o(w/s)}} = \gamma_{\mathrm{sw}} - \gamma_{\mathrm{ow}} - \gamma_{\mathrm{so}} \qquad (5)$$

$$S_{\mathrm{w(o/s)}} = \gamma_{\mathrm{so}} - \gamma_{\mathrm{ow}} - \gamma_{\mathrm{sw}} \qquad (6)$$

γ_{so}, γ_{ow}, and γ_{sw} are the interfacial tensions between solid–oil, oil–water, and solid–water, respectively. The numerical values of these could be modified using surface-active agents (detergents) so as to affect the equilibrium location of the solid at interfaces, ie,

$$\gamma_{\mathrm{so}} \geq \gamma_{\mathrm{sw}} + \gamma_{\mathrm{ow}} \qquad (7)$$

$$\gamma_{\mathrm{sw}} \geq \gamma_{\mathrm{sw}} + \gamma_{\mathrm{so}} \qquad (8)$$

$$\gamma_{\mathrm{ow}} > \gamma_{\mathrm{sw}} + \gamma_{\mathrm{so}} \qquad (9)$$

If equation 7 holds, then the solid is exclusively in the aqueous phase; equation 8 defines the condition at which the solid resides in the oil phase whereas if equation 9 is satisfied then the solid collects at the water–oil interfacial region. Figure 16 is the flow sheet of a bench-scale study that demonstrates the concept of two-liquid flotation (40).

The term flotoflocculation is used to describe the process of aggregating dispersed oil droplets by the aid of polymeric flocculants (flocculation) then subjecting them to conventional flotation. It is also used, generically, to describe situations where particles are first aggregated then floated.

5.9. Other Applications

There are a variety of flotation processes employing the principles described.

5.9.1. Skin Flotation.

Hydrophobic particles can be removed in the form of a thin, usually one particle thick layer on top of a trough, giving rise to the skin flotation process.

5.9.2. Piggyback Flotation.

This process has also been called carrier flotation. The principle is based on the flotation of fine particles adhering to others by mutual coagulation. Thus when one is floated the other, which is usually more difficult to float, is also collected.

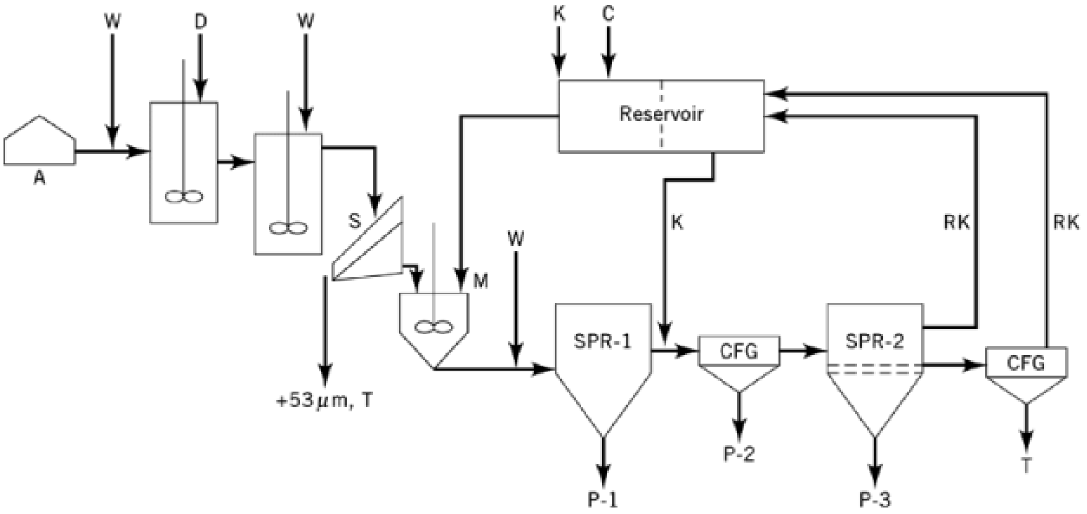

Fig. 16. Two-liquid flotation flow sheet (39). The original ROM is kaolin (white clay) that contains 11% impurity in the form of mica, anatase, and silica. Treatment produces high purity kaolin and a TiO_2-rich fraction. A, Kaolin stockpile; D, dispersant (sodium silicate plus alkali); W, water; K, kerosene; C, collector (sodium oleate); RK, recycled kerosene; S, screen; M, inline mixer; SPR, separator; CFG, centrifuge; P, product; and T, to waste.

6. Environment, Safety, and Future Developments

New technologies based on the process of froth flotation in areas outside mineral technology are being developed. These include plastics recycling, glass recycling, and recovery of radioactive contaminants or heavy-metals removal from soil; newsprint deinking is an established flotation technology. Similarly, ion and precipitate flotation as well as foam fractionation (41, 42) are areas poised for increased activity due to their potential usefulness in environmental site cleanup operations. In fact, the utilization of the unit operations and unit processes of mineral processing is fundamental to the separations technology on which recycling relies.

Ore flotation processes treat millions of tons of minerals per year, and since these are associated with mining activity they appear to be associated with physical damage to the environment. However, these technologies have a long history of practice and associated environmental control procedures. Specially lined tailings ponds, turbidity, and toxic chemical abatement approaches designed to eliminate environmental damage, as well as revegetation of old mining sites tailings ponds, dams, and dikes, are widespread practices. Furthermore, the flotation process is a technology well established in sewage treatment and water purification, and it can be used for the removal of harmful ions from effluents. Therefore it is safe and the flotation industry is self-regulating.

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