

1 Froth Flotation – Fundamental Principles

Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral/water slurry. The particles with attached air bubbles are then carried to the surface and removed, while the particles that remain completely wetted stay in the liquid phase. Froth flotation can be adapted to a broad range of mineral separations, as it is possible to use chemical treatments to selectively alter mineral surfaces so that they have the necessary properties for the separation. It is currently in use for many diverse applications, with a few examples being: separating sulfide minerals from silica gangue (and from other sulfide minerals); separating potassium chloride (sylvite) from sodium chloride (halite); separating coal from ash-forming minerals; removing silicate minerals from iron ores; separating phosphate minerals from silicates; and even non-mineral applications such as de-inking recycled newsprint. It is particularly useful for processing fine-grained ores that are not amenable to conventional gravity concentration.

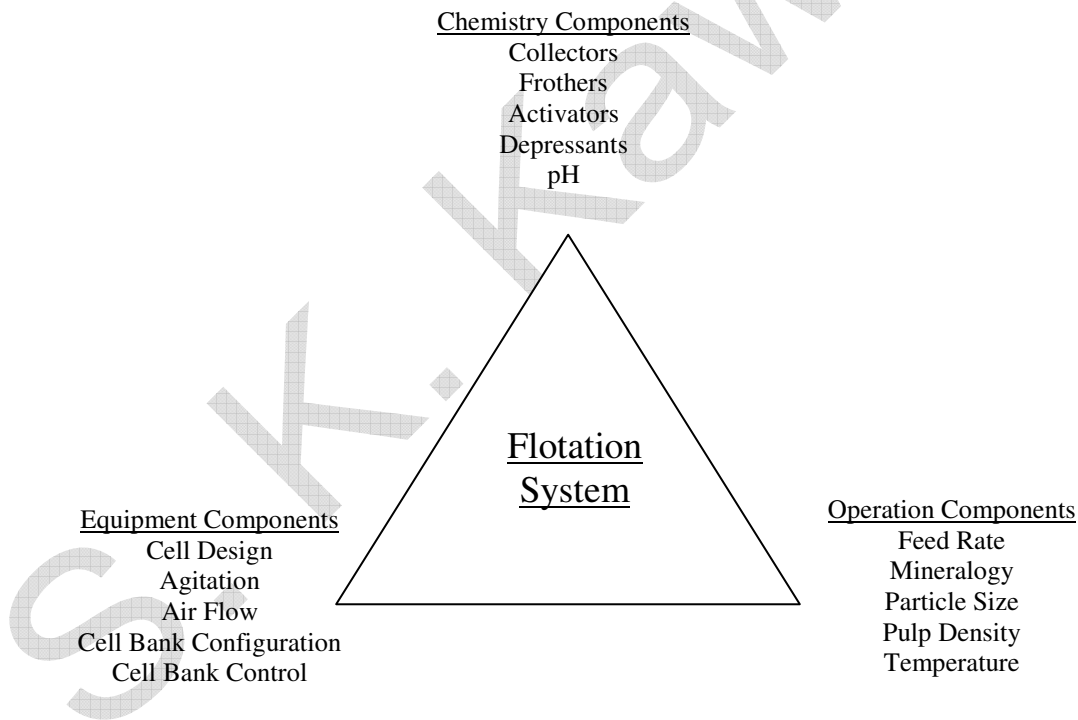


Figure 1: The flotation system includes many interrelated components, and changes in one area will produce compensating effects in other areas (Klimpel, 1995)

Froth flotation is a good example of an engineering “system”, in that the various important parameters are highly inter-related, as shown in Figure 1. It is therefore important to take all of

these factors into account in froth flotation operations. Changes in the settings of one factor (such as feed rate) will automatically cause or demand changes in other parts of the system (such as flotation rate, particle size recovery, air flow, pulp density, etc.) As a result, it is difficult to study the effects of any single factor in isolation, and compensation effects within the system can keep process changes from producing the expected effects (Klimpel, 1995). This makes it difficult to develop predictive models for froth flotation, although work is being done to develop simple models that can predict the performance of the circuit from easily-measurable parameters such as solids recovery and tailings solid content (Rao et al., 1995).

1.1 Performance Calculations

There is no one universal method for expressing the effectiveness of a separation, but there are several methods that are useful for examining froth flotation processes:

(a) Ratio of Concentration, the weight of the feed relative to the weight of the concentrate, The Ratio of Concentration is F/C , where F is the total weight of the feed and C is the total weight of the concentrate. One limitation with this calculation is that it uses the weights of the feed and concentrate. While this data is available in laboratory experiments, in the plant it is likely that the ore is not weighed and only assays will be available. However, it is possible to express the ratio of concentration in terms of ore assays. Starting with the mass balance equations, and the definition of the ratio of concentration:

$$F = C + T, \quad Ff = Cc + Tt, \quad \text{Ratio of Concentration} = F/C$$

where F , C , and T are the % weights of the feed, concentrate, and tailings, respectively; and f , c , and t are the assays of the feed, concentrate, and tailings. We now need to eliminate T from these equations so that we can solve for F/C :

$Ff = Cc + Tt$, and multiplying $(F = C + T)$ by t gives us:

$Ft = Ct + Tt$, so subtracting this equation from the previous eliminates T and gives:

$F(f - t) = C(c - t)$, and rearranging produces the equation for the ratio of concentration:

$$F/C = (c - t)/(f - t)$$

(b) % Metal Recovery, or percentage of the metal in the original feed that is recovered in the concentrate. This can be calculated using weights and assays, as $(Cc)/(Ff) \cdot 100$. Or, since $C/F = (f - t)/(c - t)$, the % Metal Recovery can be calculated from assays alone using $100(c/f)(f - t)/(c - t)$.

(c) % Metal Loss is the opposite of the % Metal Recovery, and represents the material lost to the tailings. It can be calculated simply by subtracting the % Metal Recovery from 100%.

(d) % Weight Recovery is essentially the inverse of the ratio of concentration, and equals $100 \cdot C/F = 100 \cdot (f - t)/(c - t)$.

(e) Enrichment Ratio is calculated directly from assays as c/f , weights are not involved in the calculation.

Example Calculations:

Problem: A copper ore initially contains 2.09% Cu. After carrying out a froth flotation separation, the products are as shown in Table 1. Using this data, calculate:

- (a) Ratio of concentration
- (b) % Metal Recovery
- (c) % Metal Loss
- (d) % Weight Recovery, or % Yield
- (e) Enrichment Ratio

Table 1: Grade/recovery performance of a hypothetical copper ore flotation process.

<u>Product</u>	<u>% Weight</u>	<u>% Cu Assay</u>
Feed	100	2.09
Concentrate	10	20.0
Tailings	90	0.1

(a) From Table 1, the Ratio of Concentration can be calculated as $F/C = 100/10 = 10$. If only assays are available, the ratio of concentration equals $(20 - 0.1)/(2.09 - 0.1) = 10$

So, for each 10 tons of feed, the plant would produce 1 ton of concentrate.

(b) Using the example data from Table 1, the % Cu recovery calculated from weights and assays is:

$$\% \text{ Cu Recovery} = [(10 \cdot 20)/(2.09 \cdot 100)] \cdot 100 = 95.7\%$$

The calculation using assays alone is

$$\% \text{ Cu Recovery} = 100(20/2.09)(2.09 - 0.1)/(20 - 0.1) = 95.7\%$$

This means that 95.7% of the copper present in the ore was recovered in the concentrate, while the rest was lost in the tailings.

(c) The % Cu Loss can be calculated by subtracting the % Cu Recovery from 100%:

$$\% \text{ Cu Loss} = 100 - 95.7 = 4.3\%$$

This means that 4.3% of the copper present in the ore was lost in the tailings.

(d) The % Weight Recovery is equal to the % Weight of the concentrate in Table 1. It can also be calculated from the assay values given in the table, as follows:

$$\% \text{ Weight Recovery} = 100 \cdot (2.09 - 0.1) / (20 - 0.1) = 10\%$$

(e) The Enrichment Ratio is calculated by dividing the concentrate assay in Table 1 by the feed assay:

$$\text{Enrichment Ratio} = 20.0 / 2.09 = 9.57$$

This tells us that the concentrate has 9.57 times the copper concentration of the feed.

1.1.1 Grade/Recovery Curves

While each of these single calculated values are useful for comparing flotation performance for different conditions, it is most useful to consider both the grade and the recovery simultaneously, using a “Grade/Recovery Curve”. This is a graph of the recovery of the valuable metal achieved versus the product grade at that recovery, and is particularly useful for comparing separations where both the grade and the recovery are varying. A set of grade/recovery curves is shown in Figure 2. If 100% of the feed is recovered to the product, then the product will obviously have the same composition as the feed, and so the curve starts at the feed composition with 100% recovery. Similarly, if the purest mineral grain that contains the metal of interest is removed, this will be the maximum grade that can be produced by a physical separation, and so the 0% recovery end of the curve terminates at an assay less than or equal to the assay of the purest grains available in the ore. In the graphs shown in Figure 2, points that are higher and to the right show better performance than points that are lower and to the left.

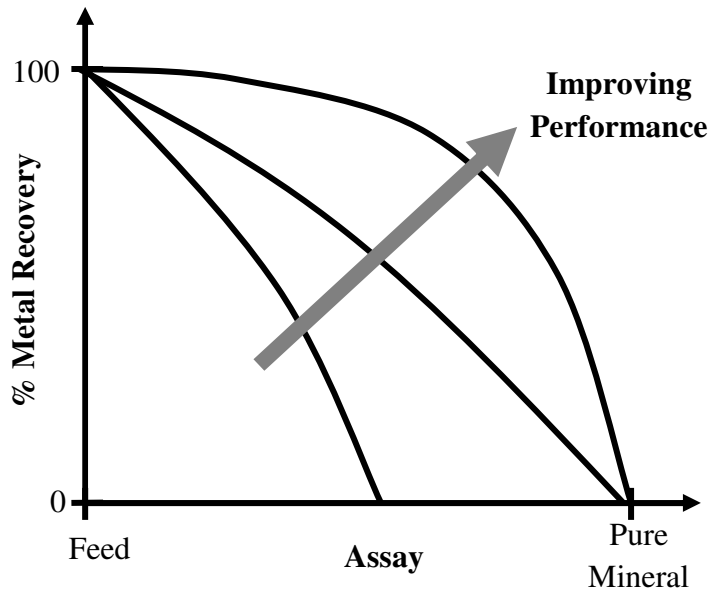


Figure 2: Typical form of Grade/Recovery Curves for froth flotation

1.2 Hydrophobicity/hydrophilicity

The basis of froth flotation is the difference in wettabilities of different minerals. Particles range from those that are easily wettable by water (hydrophilic) to those that are water-repellent (hydrophobic). If a mixture of hydrophobic and hydrophilic particles are suspended in water, and air is bubbled through the suspension, then the hydrophobic particles will tend to attach to the air bubbles and float to the surface, as shown in Figure 3. The froth layer that forms on the surface will then be heavily loaded with they hydrophobic mineral, and can be removed as a separated product. The hydrophilic particles will have much less tendency to attach to air bubbles, and so it will remain in suspension and be flushed away (Whelan and Brown, 1956).

Particles can either be naturally hydrophobic, or the hydrophobicity can be induced by chemical treatments. Naturally hydrophobic materials include hydrocarbons, and non-polar solids such as elemental sulfur. Coal is a good example of a material that is typically naturally hydrophobic, because it is mostly composed of hydrocarbons. Chemical treatments to render a surface hydrophobic are essentially methods for selectively coating a particle surface with a monolayer of non-polar oil.

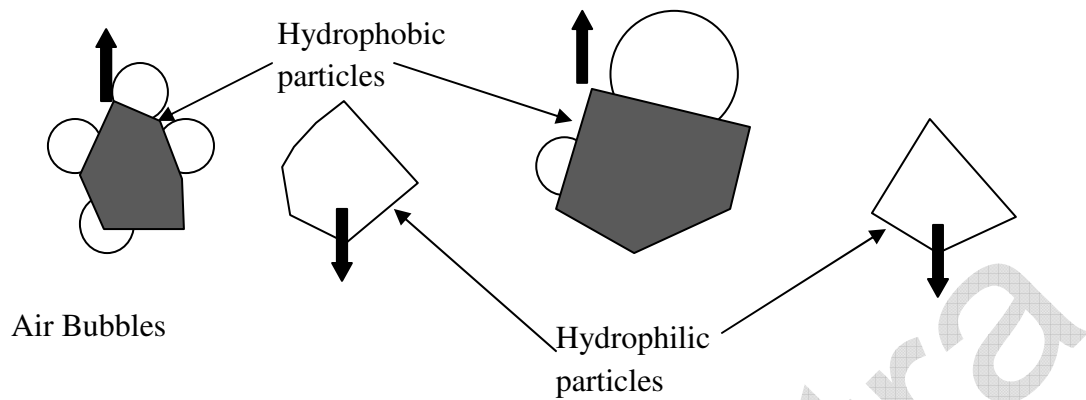


Figure 3: Selective attachment of air bubbles to hydrophobic particles. The buoyancy of the bubbles then carries these particles to the surface, leaving the hydrophilic particles behind.

The attachment of the bubbles to the surface is determined by the interfacial energies between the solid, liquid, and gas phases. This is determined by the Young/Dupre Equation,

$$\gamma_{lv}\cos\theta = (\gamma_{sv} - \gamma_{sl})$$

where γ_{lv} is the surface energy of the liquid/vapor interface, γ_{sv} is the surface energy of the solid/vapor interface, γ_{sl} is the surface energy of the solid/liquid interface, and θ is the “contact angle”, the angle formed at the junction between vapor, solid, and liquid phases, as shown in Figure 4. If the contact angle is very small, then the bubble does not attach to the surface, while a very large contact angle results in very strong bubble attachment. A contact angle near 90° is sufficient for effective froth flotation in most cases.

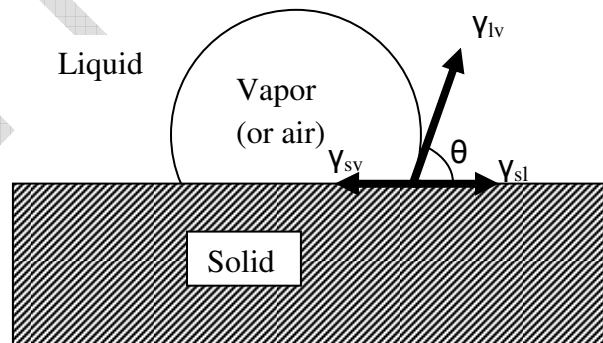


Figure 4: Contact angle between and air bubble and a solid surface immersed in liquid.

1.3 Particle/Bubble Contact

Once the particles are rendered hydrophobic, they must be brought in contact with gas bubbles so that the bubbles can attach to the surface. If the bubbles and surfaces never come in contact, then no flotation can occur. Contact between particles and bubbles can be accomplished in a flotation cell such as the one shown schematically in Figure 5.

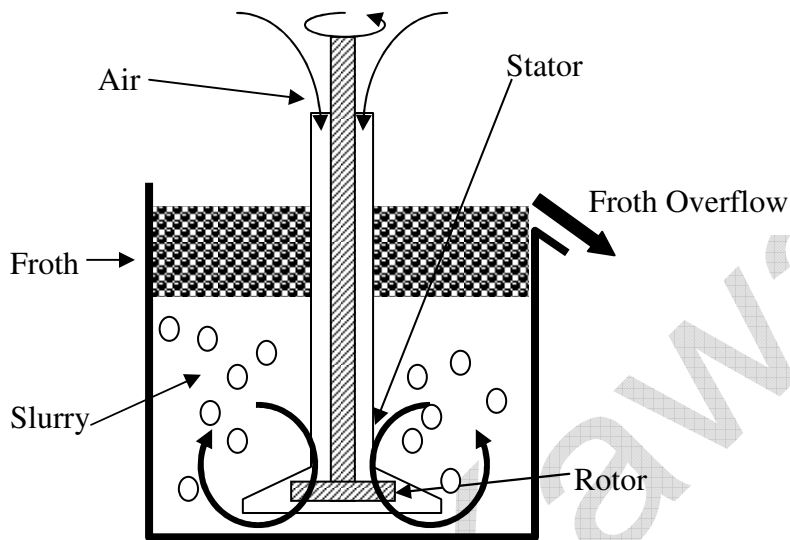


Figure 5: Simplified schematic of a conventional flotation cell. The rotor draws slurry through the stator and expels it to the sides, creating a suction that draws air down the shaft of the stator. The air is then dispersed as bubbles through the slurry, and comes in contact with particles in the slurry that is drawn through the stator.

Particle/bubble collision is affected by the relative sizes of the particles. If the bubbles are large relative to the particles, then fluid flowing around the bubbles can sweep the particles past without coming in contact. It is therefore best if the bubble diameter is comparable to the particle diameter in order to ensure good particle/bubble contact.

1.4 Collection in the Froth Layer

Once a particle and bubble have come in contact, the bubble must be large enough for its buoyancy to lift the particle to the surface. This is obviously easier if the particles are low-density (as is the case for coal) than if they are high-density (such as lead sulfide). The particle and bubble must remain attached while they move up into the froth layer at the top of the cell. The froth layer must persist long enough to either flow over the discharge lip of the cell by

gravity, or to be removed by mechanical froth scrapers. If the froth is insufficiently stable, the bubbles will break and drop the hydrophobic particles back into the slurry prematurely. However, the froth should not be so stable as to become persistent foam, as a foam is difficult to convey and pump through the plant.

The surface area of the bubbles in the froth is also important. Since particles are carried into the froth by attachment to bubble surfaces, increasing amounts of bubble surface area allows a more rapid flotation rate of particles. At the same time, increased surface area also carries more water into the froth as the film between the bubbles. Since fine particles that are not attached to air bubbles will be unselectively carried into the froth along with the water (entrainment), excessive amounts of water in the froth can result in significant contamination of the product with gangue minerals.

1.5 Reagents

The properties of raw mineral mixtures suspended in plain water are rarely suitable for froth flotation. Chemicals are needed both to control the relative hydrophobicities of the particles, and to maintain the proper froth characteristics. There are therefore many different reagents involved in the froth flotation process, with the selection of reagents depending on the specific mineral mixtures being treated.

1.5.1 Collectors

Collectors are reagents that are used to selectively adsorb onto the surfaces of particles. They form a monolayer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons. The collectors greatly increase the contact angle so that bubbles will adhere to the surface. Selection of the correct collector is critical for an effective separation by froth flotation. Collectors can be generally classed depending on their ionic charge: they can be nonionic, anionic, or cationic, as shown in Figure 6. The nonionic collectors are simple hydrocarbon oils, while the anionic and cationic collectors consist of a polar part that selectively attaches to the mineral surfaces, and a non-polar part that projects out into the solution and makes the surface hydrophobic. Collectors can either chemically bond to the mineral surface (chemisorption), or be held on the surface by physical forces (physical adsorption).

1.5.1.1 Chemisorption

In chemisorption, ions or molecules from solution undergo a chemical reaction with the surface, becoming irreversibly bonded. This permanently changes the nature of the surface.

Chemisorption of collectors is highly selective, as the chemical bonds are specific to particular atoms.

1.5.1.2 Physisorption

In physisorption, ions or molecules from solution become reversibly associated with the surface, attaching due to electrostatic attraction or van der Waals bonding. The physisorbed substances can be desorbed from the surface if conditions such as pH or composition of the solution changes. Physisorption is much less selective than chemisorption, as collectors will adsorb on any surface that has the correct electrical charge or degree of natural hydrophobicity.

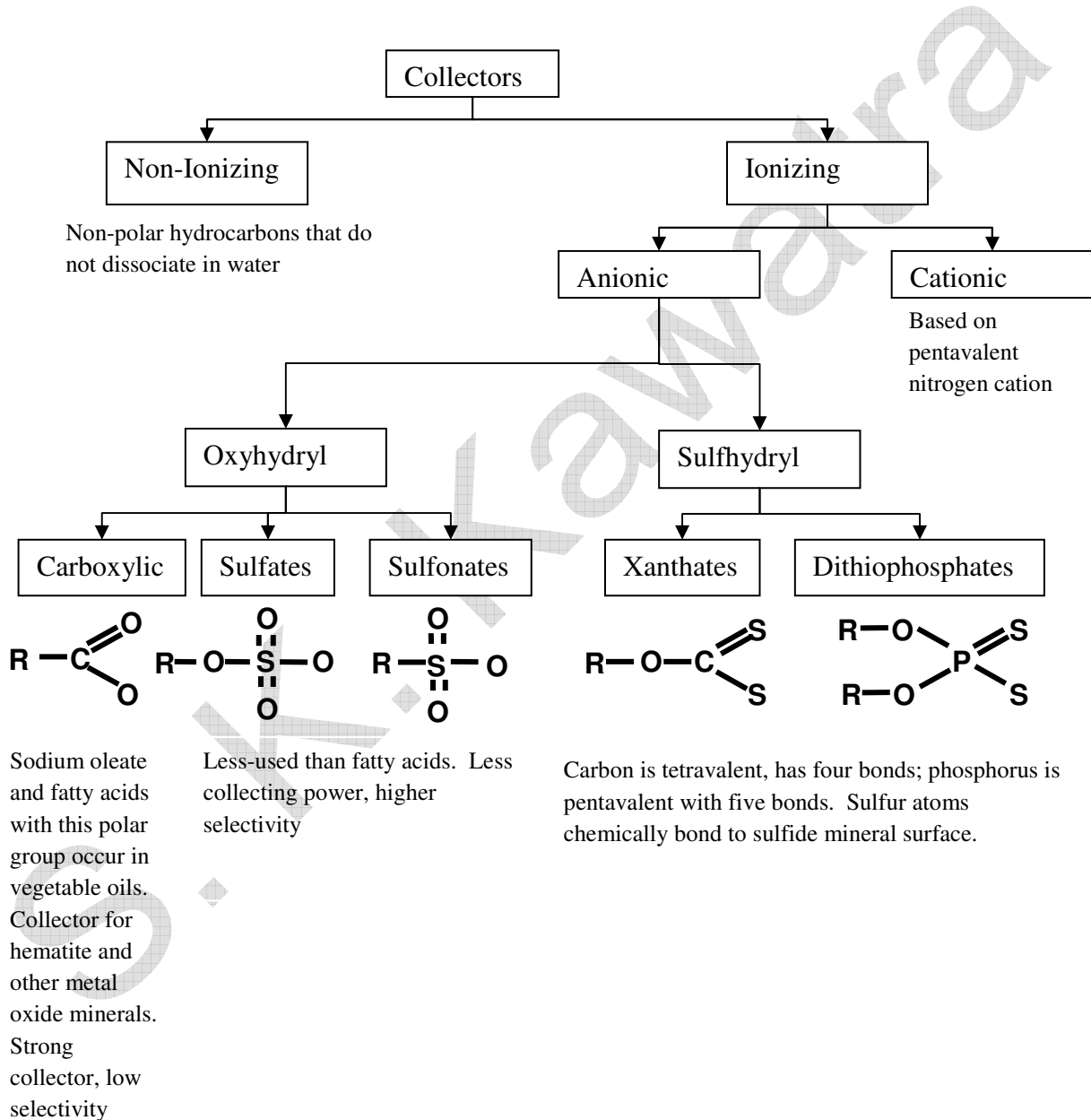


Figure 6: Basic collector types, after Glembotskii et al. (1972). In the structures, “R” represents a hydrocarbon chain, different collectors will use different hydrocarbons for “R”

1.5.1.3 Nonionic Collectors

Hydrocarbon oils, and similar compounds, have an affinity for surfaces that are already partially hydrophobic. They selectively adsorb on these surfaces, and increase their hydrophobicity. The most commonly-floated naturally-hydrophobic material is coal. Addition of collectors such as #2 fuel oil and kerosene significantly enhances the hydrophobicity of the coal particles without affecting the surfaces of the associated ash-forming minerals. This improves the recovery of the coal, and increases the selectivity between coal particles and mineral matter. Fuel oil and kerosene have the following advantages over specialized collectors for froth flotation: 1) they have low enough viscosity to disperse in the slurry and spread over the coal particles easily, and 2) they are very low-cost compared to other compounds which can be used as coal collectors.

In addition to coal, it is also possible to float naturally-hydrophobic minerals such as molybdenite, elemental sulfur, and talc with nonionic collectors. Nonionic collectors can also be used as “extenders” for other collectors. If another, more-expensive collector makes a surface partially hydrophobic, adding a nonpolar oil will often increase the hydrophobicity further at low cost.

1.5.1.4 Anionic Collectors

Anionic collectors are weak acids or acid salts that ionize in water, producing a collector that has a negatively-charged end that will attach to the mineral surfaces, and a hydrocarbon chain that extends out into the liquid, as shown in Figure 7.

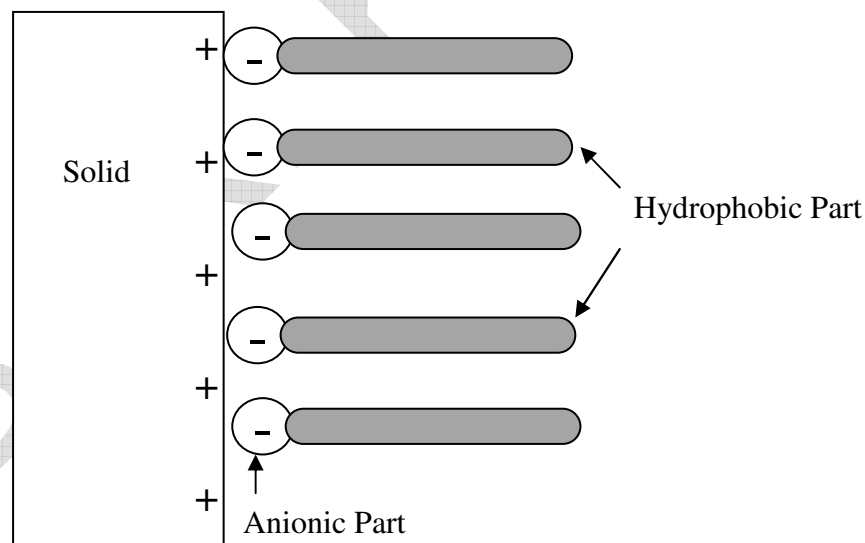


Figure 7: Adsorption of anionic collector onto a solid surface. The anionic portion is responsible for the attachment of the collector molecule to the surface, while the hydrophobic part alters the surface hydrophobicity.

1.5.1.4.1 Anionic Collectors for Sulfide Minerals

The most common collectors for sulfide minerals are the sulfhydryl collectors, such as the various xanthates and dithiophosphates. Xanthates are most commonly used, and have structures similar to what is shown in Figure 8. Xanthates are highly selective collectors for sulfide minerals, as they chemically react with the sulfide surfaces and do not have any affinity for the common non-sulfide gangue minerals. Other highly-selective collectors for use with sulfide minerals, such as dithiophosphates, have somewhat different adsorption behavior and so can be used for some separations that are difficult using xanthates.

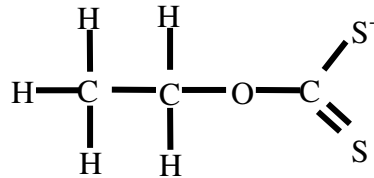


Figure 8: Structure of a typical xanthate collector (ethyl xanthate). The OCSS⁻ group attaches irreversibly to the sulfide mineral surface. Using xanthates with longer hydrocarbon chains tends to increase the degree of hydrophobicity when they adsorb onto the surface.

1.5.1.4.2 Anionic Collectors for Oxide Minerals

The collectors available for flotation of oxide minerals are not as selective as the collectors used for sulfide mineral flotation, as they attach to the surface by electrostatic attraction rather than by chemically bonding to the surface. As a result, there is some collector adsorption onto the minerals that are not intended to float.

A typical anionic collector for oxide mineral flotation is sodium oleate, the sodium salt of oleic acid, which has the structure shown in Figure 9. The anionic group responsible for attaching it to the mineral surface is the carboxyl group, which dissociates in water to develop a negative charge. The negatively-charged group is then attracted to positively-charged mineral surfaces.

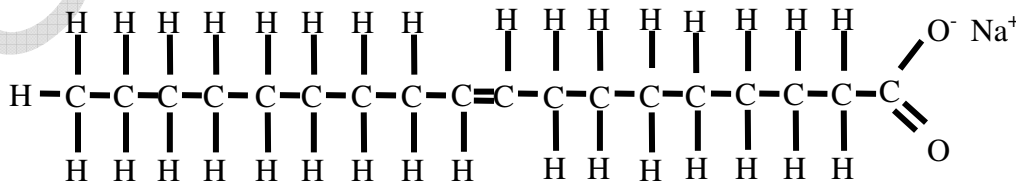


Figure 9: The structure of oleic acid, a very commonly-used anionic collector.

Since particles that are immersed in water develop a net charge due to exchanging ions with the liquid, it is often possible to manipulate the chemistry of the solution so that one mineral has a strong positive charge while other minerals have a charge that is either only weakly positive, or negative. In these conditions, the anionic collector will preferentially adsorb onto the surface with the strongest positive charge and render them hydrophobic.

1.5.1.5 Cationic Collectors

Cationic collectors use a positively-charged amine group (shown in Figure 10) to attach to mineral surfaces. Since the amine group has a positive charge, it can attach to negatively-charged mineral surfaces. Cationic collectors therefore have essentially the opposite effect from anionic collectors, which attach to positively-charged surfaces. Cationic collectors are mainly used for flotation of silicates and certain rare-metal oxides, and for separation of potassium chloride (sylvite) from sodium chloride (halite).

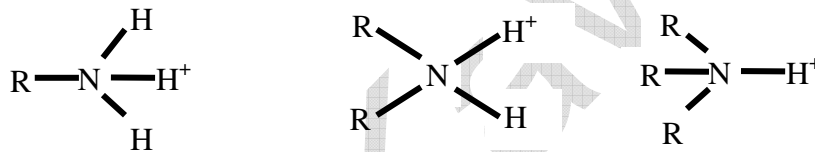


Figure 10: Primary, secondary, and tertiary amine groups that can be used for cationic collectors.

1.5.2 Frothers

Frothers are compounds that act to stabilize air bubbles so that they will remain well-dispersed in the slurry, and will form a stable froth layer that can be removed before the bubbles burst. The most commonly used frothers are alcohols, particularly MIBC (Methyl Isobutyl Carbinol, or 4-methyl-2-pentanol, a branched-chain aliphatic alcohol) or any of a number of water-soluble polymers based on propylene oxide (PO) such as polypropylene glycols. The polypropylene glycols in particular are very versatile, and can be tailored to give a wide range of froth properties. Many other frothers are available, such as cresols and pine oils, but most of these are considered obsolete and are not as widely used as they once were. Some work has also been done using salt water (particularly seawater) as the frothing agent, and the process has been used industrially in Russia (Klassen and Mokrousov, 1963; Tyurnikova and Naumov, 1981).

1.5.2.1 Function of Frothers

Klimpel (1995) found that use of different frothers produced changes in the flotation rate (K) and recovery (R) values in coal flotation, and reached the following conclusions:

- When frother dosage was held constant while collector dosage was increased, it was found that the flotation rate went through a maximum and then decreased. This was observed for all frother types and all particle size fractions. The difference between the frother families studied was that the collector dosage that produced the maximum value of K was different.
- For all of the frother types, the finest (-88 μm) and coarsest (+500 μm) particles tended to float more slowly than the intermediate-size particles.
- Changes in flotation rate were due to both changes in the coal particle size, and to frother/collector dosage. While the contribution of particle size was generally more significant, the reagent dosage effect provides a useful means for adjusting K in the plant.
- With aliphatic alcohol frothers, the flotation rate maximum was much more pronounced than for the Propylene Oxide (PO) and combined Propylene Oxide/Alcohol (PO-Alcohol Adduct) frothers.
- Regardless of frother type, increasing the frother dosage to increase recovery always leads to less selective flotation.
- The PO and PO-Alcohol Adduct frothers are more powerful recovery agents than alcohol frothers, and therefore should be used at lower dosages.
- Over-dosing with alcohol frothers leads to a slower flotation rate, because excesses of these frothers tend to destabilize the froth. This effect does not occur with the PO and PO-Alcohol frothers, and so overdosing with these frothers leads to high recovery with poor selectivity.
- PO frothers with molecular weights of 300 to 500 are optimal for coal recovery.
- Alcohol frothers tend to be more effective for fine-particle recovery than for coarse-particle recovery. To recover coarse particles, the alcohol frother and the hydrocarbon collector dosages should both be high. The alcohol will still provide reasonable selectivity at these high dosages.
- The high-molecular-weight PO-based frothers are more effective for coarse particle flotation than the alcohol or low-molecular-weight PO frothers, but also have a lower selectivity. For both good coarse-particle recovery and good selectivity, the PO frothers should be used at low dosage, with low collector dosage as well. The PO-Alcohol Adduct frothers are even more effective for coarse-particle recovery, and need to be used at even lower dosages.

- The optimal frother for high recovery with good selectivity will often be a blend of members of the various frother classes examined. It is reported that such frother blending will give enough benefit to be worth the effort in approximately half of all coal flotation operations.
- None of the frothers in the three categories studied will change the shape of the grade/recovery curve. Changes in frother type and dosage simply move the flotation results along the curve. Similarly, changes in hydrocarbon collector dosage also mainly move the performance along the grade/recovery curve.
- For medium and coarse coal size fractions, the total gangue recovered is linearly related to the total coal recovered. It is only for the finest particles that the gangue recovery increases non-linearly with increasing coal recovery.
- When floating coals with a broad particle size range, the majority of the gangue reaching the froth is from the finer particle size fractions.
- As the rate of coal flotation increases, the rate of gangue flotation increases proportionately. This is typical of a froth entrainment process acting on the gangue.

1.5.2.2 Synthetic and Natural Frothers

The original frothers were natural products, such as pine oil and cresylic acid. These are rich in surface-active agents that stabilize froth bubbles, and are effective frothers. As natural products, they are not pure chemicals, but instead contain a broad range of chemicals other than those that are effective frothers. Some of these compounds can act as collectors by attaching to mineral surfaces. As a result, these frothers are also weak collectors. While this can have the advantage of reducing the amount of collector that needs to be added separately, it introduces some problems with process control. If the frother is also a collector, then it becomes impossible to alter the frothing characteristics and the collecting characteristics of the flotation operation independently.

Synthetic frothers, such as the alcohol-type and polypropylene glycol-type frothers, have the advantage that their effectiveness as collectors is negligible. It is therefore possible to increase the frother dosage without also changing the quantity of collector in the system. This in turn makes the flotation process much easier to control.

1.5.3 Modifiers

Modifiers are chemicals that influence the way that collectors attach to mineral surfaces. They may either increase the adsorption of collector onto a given mineral (activators), or prevent collector from adsorbing onto a mineral (depressants). It is important to note that just because a reagent is a depressant for one mineral/collector combination, it does not necessarily follow that

it is a depressant for other combinations. For example, sodium sulfide is a powerful depressant for sulfide minerals being floated with xanthate, but does not affect flotation when sulfide minerals are floated with the collector hexadecyl trimethyl ammonium bromide.

1.5.3.1 pH Control

The simplest modifiers are pH control chemicals. The surface chemistry of most minerals is affected by the pH. For example, in general minerals develop a positive surface charge under acidic conditions and a negative charge under alkaline conditions. Since each mineral changes from negatively-charged to positively-charged at some particular pH, it is possible to manipulate the attraction of collectors to their surfaces by pH adjustment. There are also other, more complex effects due to pH that change the way that particular collectors adsorb on mineral surfaces.

Sulfhydryl collectors such as xanthate ions compete with OH^- ions to adsorb on mineral surfaces, and so adsorption is a function of pH. This makes it possible for sulfhydryl collectors to be used to progressively separate specific minerals. The pH where the xanthate ion wins the competition with OH^- ions depends both on the concentration of xanthate in solution, and on the specific sulfide mineral present, as shown in Figure 11.

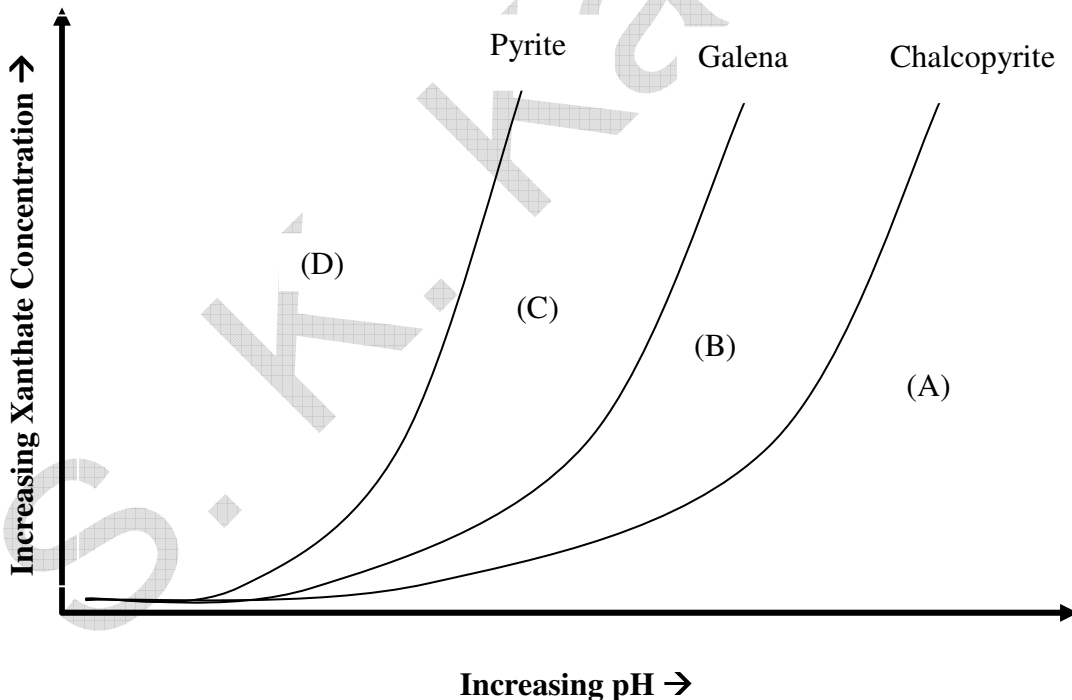


Figure 11: Schematic of the pH response curves for sulfhydryl collector adsorption on different sulfide minerals. These curves mark the boundary where the given mineral becomes sufficiently hydrophobic to float. Both xanthates and dithiophosphates exhibit curves of this form, with different pH values and concentrations for each type of collector (Fuerstenau et al., 1985).

For example, assume a mixture of pyrite (FeS_2), galena (PbS), and chalcopyrite (CuFeS_2). From Figure 11, we see that if the pH and xanthate concentrations are in region (A), then xanthate does not adsorb on any of the minerals and no minerals float. If the pH and xanthate concentrations are altered to move into region (B), then only chalcopyrite becomes hydrophobic and floats. In region (C), both chalcopyrite and galena will float, and in region (D) all three minerals will float. It is therefore possible to progressively lower the pH to float first chalcopyrite, then galena, and then pyrite, producing concentrates for each mineral and leaving behind any non-floatable silicate gangue minerals.

1.5.3.1.1 Acids

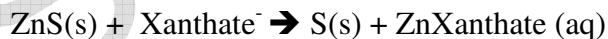
The acids used are generally those that give the greatest pH change at the lowest cost, with sulfuric acid being most popular. A key point to keep in mind is that the anion of the acid can potentially have effects of its own, separate from the lowering of the pH. There are therefore some cases where acids other than sulfuric acid are useful.

1.5.3.1.2 Alkalis

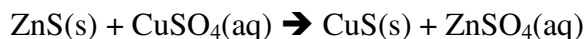
Like acids, the most popular alkalis are those that are cheapest, with the lowest-cost alkali generally being lime (CaO or $\text{Ca}(\text{OH})_2$). However, the calcium ion often interacts with mineral surfaces to change their flotation behavior. In some cases the calcium ions have beneficial effects, while in other cases they change the flotation in undesirable ways. It may therefore be necessary to use sodium-based alkalis such as NaOH or Na_2CO_3 , because the sodium cation generally does not have any significant effect on the particle surface chemistries.

1.5.3.2 Activators

Activators are specific compounds that make it possible for collectors to adsorb onto surfaces that they could not normally attach to. A classic example of an activator is copper sulfate as an activator for sphalerite (ZnS) flotation with xanthate collectors (Fuerstenau et al., 1985). When untreated, xanthate cannot attach to the sphalerite surface because it forms a zinc-xanthate compound that quickly dissolves:



The surface of the sphalerite can be activated by reacting it with a metal ion that does not form a soluble xanthate, such as soluble copper from dissolved copper sulfate:



This forms a thin film of copper sulfide on the sphalerite surface, which allows for stable attachment of the xanthate, rendering the sphalerite particle hydrophobic and floatable. Other

metals such as silver and lead can also be used to activate zinc, but copper is cheaper than silver and less toxic than lead.

It is also possible to adsorb specific ions onto the surface that can promote attachment of the collector. For example, silica (SiO_2) normally has a strongly-negative surface charge at approximately neutral pH, and therefore has little affinity for anionic collectors such as oleic acid. However, calcium ions specifically adsorb onto silica surfaces, and the negative charge of the calcium ions can actually reverse the surface charge, making it positive. It is then possible for the anionic collectors to electrostatically attach to the calcium-activated silica surface.

1.5.3.3 Depressants

Depressants have the opposite effect of activators, by preventing collectors from adsorbing onto particular mineral surfaces. Their typical use is to increase selectivity by preventing one mineral from floating, while allowing another mineral to float unimpeded.

1.5.3.3.1 *Cyanide*

Cyanide (CN^-) is a particularly useful depressant in sulfide mineral flotation. Its activity is believed to be due to its ability to complex with, and in some cases dissolve, a number of metal ions, preventing them from attaching to the xanthate molecules. In particular, it is a strong depressant for pyrite (FeS_2), and can be used to “deactivate” sphalerite that has been activated by copper ions in solution (Fuerstenau et al, 1985).

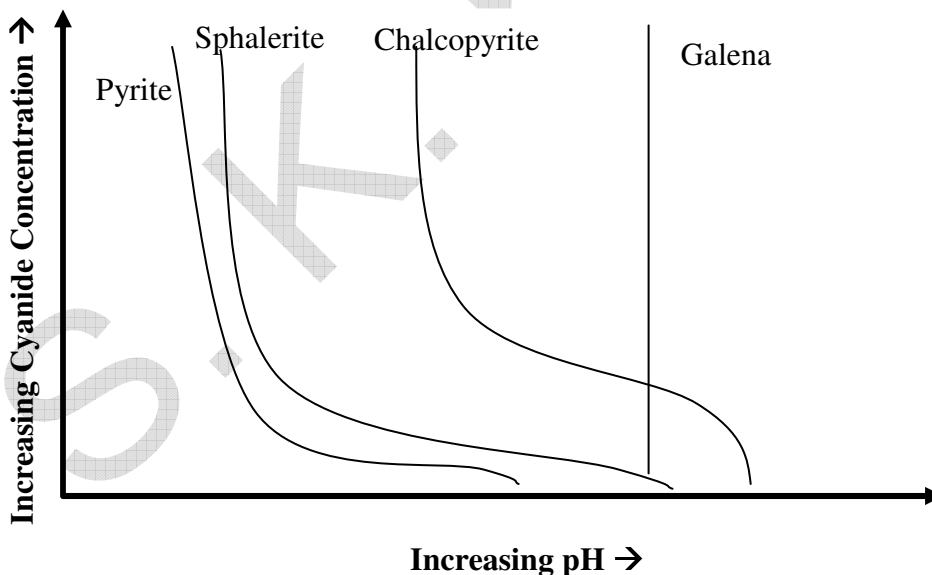


Figure 12: Effect of cyanide depressant on flotation of minerals as a function of pH. It is interesting to note that flotation of galena (PbS) is unaffected by the presence of cyanide.

1.5.3.3.2 Lime

Lime is added as either CaO or Ca(OH)₂, and when it dissolves it contributes calcium ions that can adsorb onto mineral surfaces. In combination with its strong alkaline nature, this makes it particularly useful in manipulating sulfide flotation. It is less useful in oxide mineral flotation, because it can activate the flotation of silica by anionic collectors, causing it to float along with the other oxide minerals

1.5.3.3.3 Organic Depressants

A large number of organic compounds are useful as flotation depressants. These tend to be soluble polymers (such as starch) that selectively coat mineral surfaces and prevent collector from attaching. An example of this is in the “reverse flotation” of silica from iron ore, where the silica tailings are floated using a cationic collector at a pH of 8.5 - 11, leaving behind the iron oxide minerals. Starch acts as a depressant for iron oxide in this process, preventing it from being floated by the cationic collector.

1.5.4 Recovery of Gangue Particles in Flotation: Entrainment or Hydrophobicity?

There is always some gangue material that is recovered in the froth. For example, in flotation of coal, a portion of the ash-forming minerals and pyrite will be carried into the froth along with the coal. It is common to believe that this gangue mineral can be prevented from floating if only the correct depressant can be discovered. In the case of coal, over 42 different chemicals have been reported by many investigators to depress pyrite flotation, and yet none of them have ever been useful industrially. This is because, in most cases, the pyrite was not truly hydrophobic in the first place (Kawatra and Eisele, 1992, 2001)

In a froth flotation machine, there are two ways that a particle can reach the froth layer. It can be carried into the froth by attachment to an air bubble (true flotation), or it can be suspended in the water trapped between the bubbles (entrainment). While true flotation is selective between hydrophobic and hydrophilic particles, entrainment is nonselective, and so entrained particles are just as likely to be gangue minerals as they are to be the valuable mineral. If particles are sufficiently coarse, then they settle rapidly enough that they are not carried into the froth by entrainment. As they become finer, particles settle more slowly and so have more time to be entrapped in the froth, and have less tendency to drain away. Clay particles in particular, which are only a few micrometers in size, are very easily entrained. For particles that are less than a few micrometers in size, their rate of recovery into the froth by entrainment is equal to the rate of recovery of water into the froth. For example, if 20% of the water entering a flotation cell is carried into the froth, then up to 20% of the fine particles entering the cell will be entrained. The entrainment of coarser particles will be less than 20%, due to their greater ability to drain from the froth.

In addition to the entrained particles, gangue is carried into the froth by being physically locked to the floatable particles. In the case of coal, much of the pyrite consists either of sub-micron pyrite grains that are never liberated from the coal, or of pyrite particles whose surfaces consist primarily of coal, and therefore behave as if they were coal particles. The recovery of entrained particles can only be reduced by lowering the fraction of the water recovered into the froth. The recovery of locked particles can only be changed significantly by either grinding to a finer size to improve liberation, or by rejecting the locked particles along with the least-floatable liberated particles, which sacrifices recovery of the valuable mineral. Depressant chemicals are not useful in either of these cases, as they are only useful for preventing the hydrophobic bubble attachment and true flotation of particles. Before deciding to use a depressant, it is therefore important to first determine whether the particles to be depressed are actually being recovered by true flotation in the first place, or whether there are other causes.

1.6 Equipment

In addition to controlling the chemistry, flotation requires a machine for mixing and dispersing air throughout the mineral slurry while removing the froth product. These individual machines are then connected to form a flotation circuit in order to fully clean the product.

1.6.1 Conventional Cells

Conventional flotation cells consist of a tank with an agitator designed to disperse air into the slurry, as was previously shown schematically in Figure 5. These are relatively simple machines, with ample opportunity for particles to be carried into the froth along with the water making up the bubble films (entrainment), or for hydrophobic particles to break free from the froth and be removed along with the hydrophilic particles. It is therefore common for conventional flotation cells to be assembled in a multi-stage circuit, with “rougher”, “cleaner”, and “scavenger” cells, which can be arranged in configurations such as the one shown in Figure 12.

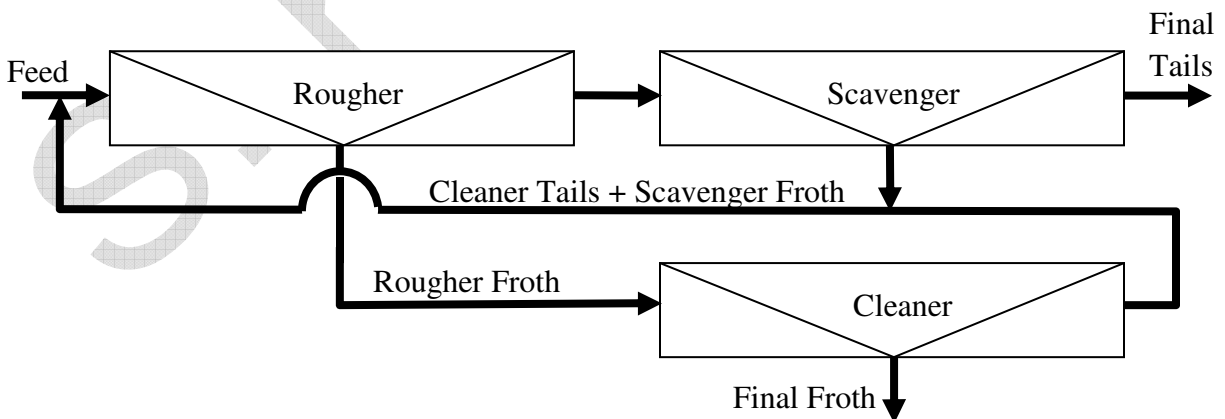


Figure 12: One possible configuration for a Rougher/Cleaner/Scavenger flotation circuit.

1.6.2 Flotation Columns

Flotation columns provide a means for improving the effectiveness of froth flotation (Eberts, 1986). A column essentially performs as if it were a multistage flotation circuit arranged vertically (Degner and Sabey, 1985), with slurry flowing downward while the air bubbles travel upward, producing a countercurrent flow. The first flotation machine design to use a countercurrent flow of slurry and air was developed by Town and Flynn in 1919. It was not until the work of Boutin and Tremblay in the early 1960's that a new generation of countercurrent columns was developed that ultimately became industrially successful (Rubinstein, 1995).

A typical flotation column is shown in Figure 13. The basic principle of column flotation is the use of countercurrent flow of air bubbles and solid particles. This is achieved by injecting air at the base of the column, and feed near the midpoint. The particles then sink through a rising swarm of air bubbles.

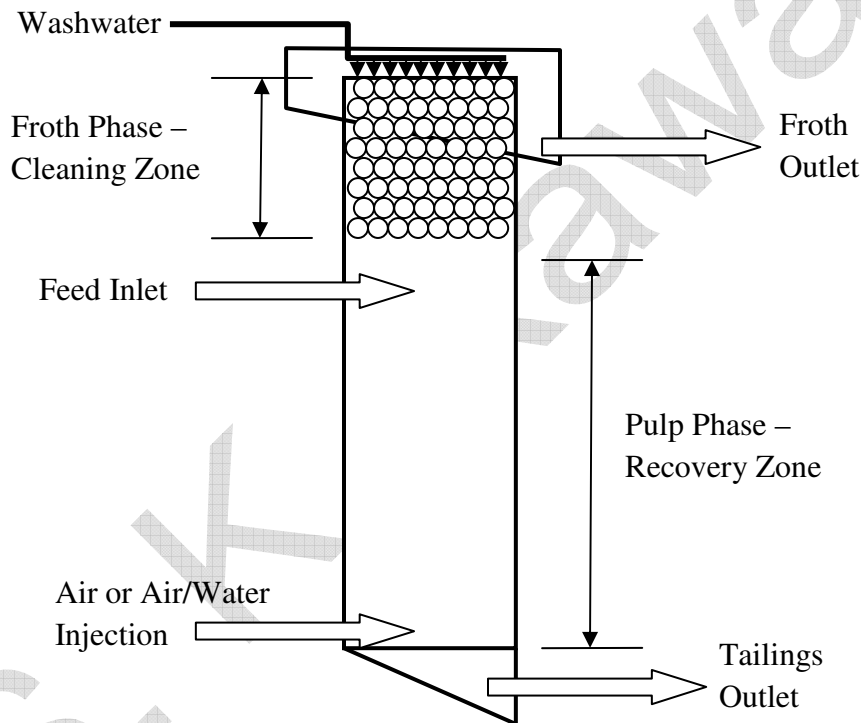


Figure 13: Schematic of a flotation column

Countercurrent flow is accentuated in most columns by the addition of washwater at the top of the column, which forces all of the water which entered with the feed downward, to the tailings outlet. This flow pattern is in direct contrast to that found in conventional cells, where both the air and the solid particles are driven in the same direction. The result is that columns provide improved hydrodynamic conditions for flotation, and thus produce a cleaner product while

maintaining high recovery and low power consumption. The performance differences between columns and conventional cells may best be described in terms of the following factors: collection zone size, particle/bubble contact efficiency, and fines entrainment (Kawatra and Eisele, 1987).

The collection zone is the volume where particle/bubble contact occurs, and it differs greatly in size between column and conventional flotation. In conventional cells, contact occurs primarily in the region surrounding the mechanical impeller. The remainder of the cell acts mainly as a storage volume for material which has not yet been through the collection zone. This creates a bottleneck which keeps the flotation rate down. In contrast, flotation columns have a collection zone which fills the entire volume of the machine, so that there are more opportunities for particle/bubble collisions. The reduced level of turbulence needed to achieve a good rate of recovery in columns also reduces the tendency of coarse particles to be torn away from the bubbles which they attach to, and therefore columns are more effective for floating coarser particles (Kawatra and Eisele, 2001).

Columns exhibit higher particle/bubble contact efficiency than conventional machines, due to the particles colliding with the bubbles head-on. As a result, the energy intensity needed to promote contact is less, and so power consumption is reduced.

A second beneficial effect in certain types of flotation columns is the reduction of bubble diameter (Yoon and Luttrell, 1986). As bubble diameter is reduced, the flotation rate of both the coarser and finer particles is improved. The effects producing the improvement are illustrated in Figure 14. Coarse particles can attach to more than one bubble if the bubbles are small, and therefore the chances of the particle being torn loose and sinking again is reduced. For fine particles, the probability of collision with the bubble is improved if the bubble is small, as then the hydrodynamic forces tending to sweep the particle away from a collision are reduced. The reduction of bubble diameter has the added benefit of increasing the available bubble surface area for the same amount of injected air. It is therefore desirable to produce bubbles as fine as possible.

The entrainment of fine waste material in the froth product is a serious failing of conventional flotation machines. It results from the need for a certain amount of water to be carried into the froth as the film surrounding the air bubbles. As a result, fine suspended particles are swept into the froth with this water, even though they are not physically attached to the air bubbles. In most column flotation machines, the entrainment problem is addressed through the use of washwater, as shown in Figure 15. Where the conventional cell must allow a certain amount of feed water to enter the froth, the washwater in the column cell displaces this feed water to the tailings, thus preventing entrained contaminants from reaching the froth. The only drawback to the use of froth washing is that the demand for clean water is increased, which may cause water problems in some situations.

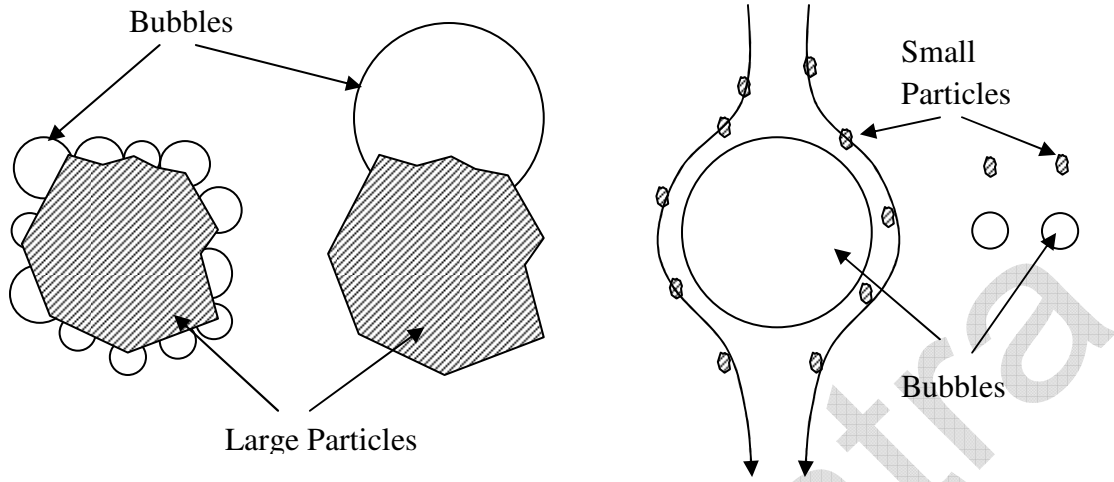


Figure 14: Effects of relative bubble and particle sizes on froth flotation.

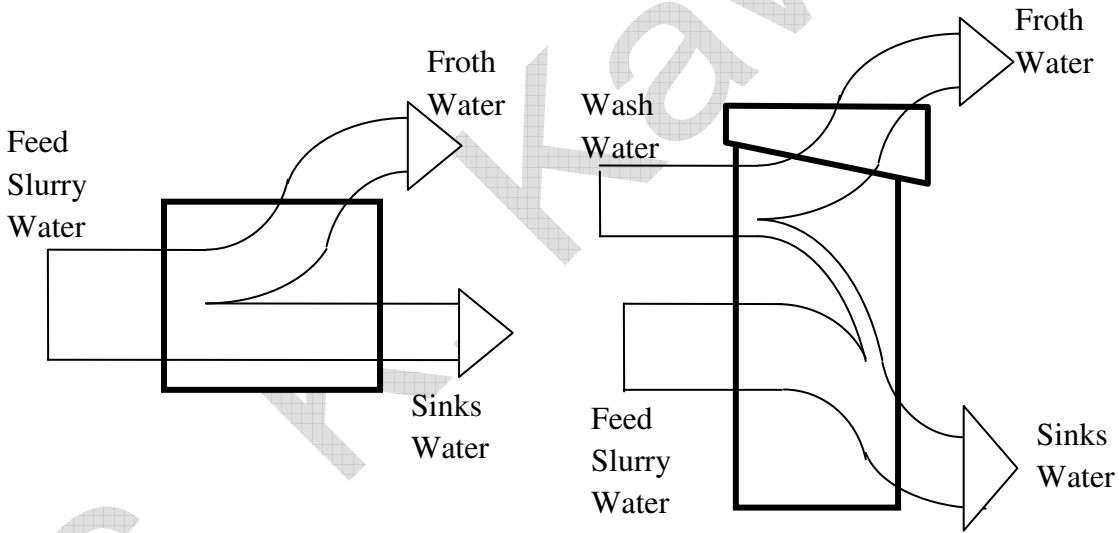


Figure 15: Effect of washwater on the entrainment of feed into the froth.

The net effect of the relatively gentle mixing, countercurrent flow, and use of washwater in columns is that there is a distance of several meters between the clean coal discharging in the froth and the concentrated gangue discharging at the tailings, with a gradual gradient of concentration between the two extremes. There is therefore a reduced possibility of coal being misplaced into the tails, or of gangue short-circuiting to the froth. The result is that a column is

typically equivalent to between three and five stages of conventional flotation, depending on the column design

1.6.2.1 Bubble Generators

The impeller-type mixers that are used in conventional cells are not well-suited for use in flotation columns, as they would either need excessively long shafts or rotating seals. In the original flotation column design, bubbles were produced using sintered ceramic air diffusers which produced very fine air bubbles. However, this was found to suffer from plugging problems, particularly in hard water, and so cloth and perforated rubber sheeting were adopted instead (Dobby et al., 1985; Boutin and Wheeler, 1967). These still required excessive maintenance, and so external bubble generators of various types have been adopted (McKay et al., 1988; Yoon et al., 1990; Rubinstein, 1995; Davis et al., 1995). The external bubble generators combine a stream of water with air to produce a mixture of very fine bubbles in water. This mixture is injected into the column. This approach has a number of advantages, including: (1) The bubble generator is accessible for adjustment and maintenance; (2) There is no porous element inside the column to clog or become damaged, and so the dispersion of air in the column does not change; (3) The bubble generator can be designed to tolerate particulate matter in the water, and so recycle water can be used in the generators; and (4) External bubble generators can consistently produce very small bubbles in the column.

1.6.2.2 Axial Mixing Effects

A key issue in flotation column operation is “axial mixing”, which is mixing along the vertical axis of the column, as shown in Figure 16. As the air bubbles rise in the column, they carry a portion of the water up with them to the base of the froth layer. The water then descends again, setting up a strong mixing action. This tendency is greatest if the column is slightly tilted from vertical, as then the bubbles preferentially ascend on one side while the water descends on the other. This is why it is particularly crucial for flotation columns to be perfectly vertical. The tendency towards axial mixing is also increased if some large bubbles are present, and so performance is best if the bubbles are uniformly small in diameter.

Another approach to suppressing axial mixing is the introduction of horizontal baffles, made from perforated plates (Kawatra and Eisele, 2001). These baffles interrupt the flow of the liquid as shown in Figure 16, preventing it from being rapidly carried to the surface, or from short-circuiting directly to the tailings. Experiments with horizontal baffles in a flotation column have confirmed that they can greatly improve the operating characteristics of the column without sacrificing capacity, and a sufficiently open baffle design is highly resistant to plugging by coarse particles or debris. Overall, flotation columns generally have superior performance to conventional flotation cells. However, they fundamentally require automatic control, as they are not well-suited for use of the simple tailings overflow weirs which are commonly used for maintaining a constant pulp level in conventional flotation cells.

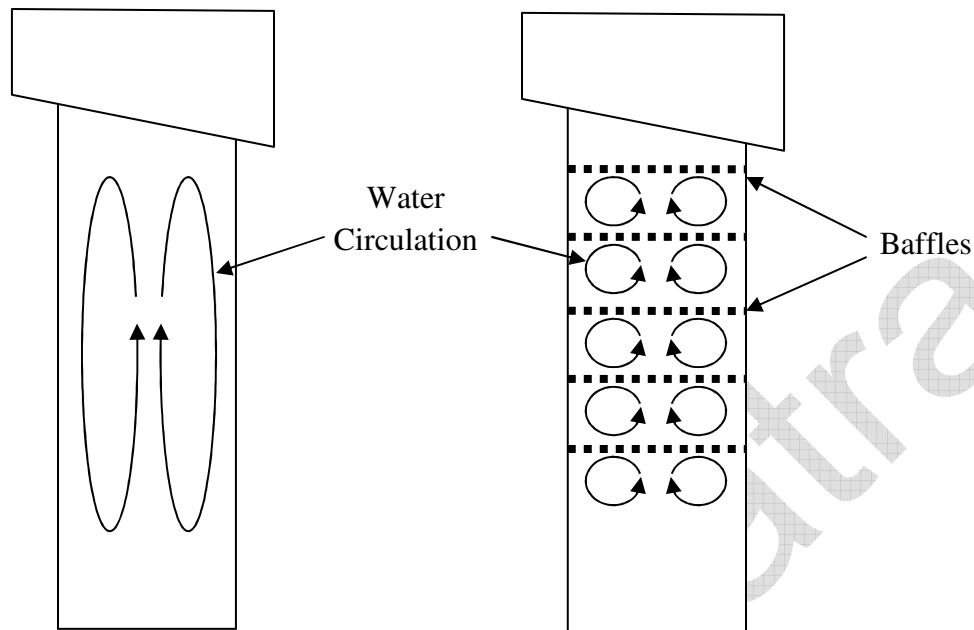


Figure 16: Comparison of axial mixing in regular columns, and horizontally-baffled columns.

1.6.3 Release Analysis

It is often useful to be able to determine the theoretical maximum amount of upgrading that can be achieved by froth flotation, given a specific ore and a particular set of reagents. One approach to this is “release analysis”, which is carried out by progressively re-floating froth products to collect only the particles that are fully hydrophobic. The procedure is illustrated in Figure 17.

Release analysis provides a means for comparing the performance of conventional flotation with column flotation. The product from release analysis is typically much higher-grade than the product from a single stage of conventional flotation. On the other hand, a correctly-operating flotation column will typically provide a product grade that is comparable to the grade of the product from the final stages of release analysis.

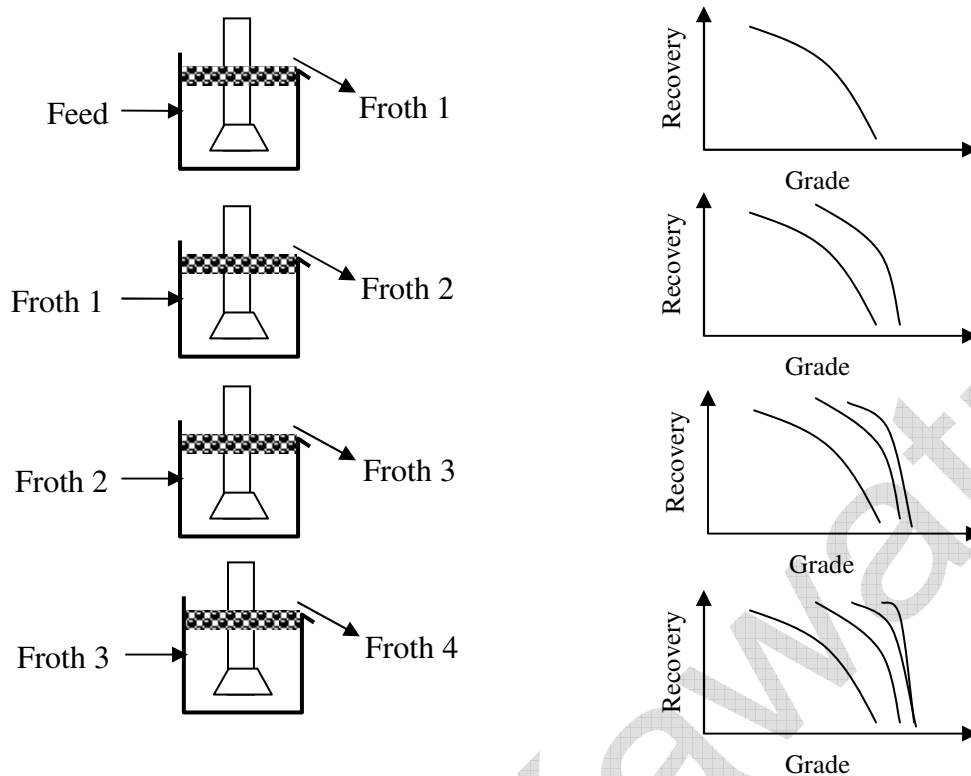


Figure 17: Illustration of the “release analysis” method for determining the maximum grade of material that can be produced by a froth flotation process. Each stage of flotation removes more of the entrained and poorly floatable particles from the froth, until the final froth product consists only of the most strongly-floatable material.

1.7 Applying Laboratory Results to Plant Equipment Selection

1.7.1 Laboratory and plant flotation kinetics

In order to compare froth flotation experiments in the laboratory with operations in the plant, it is necessary to take into account the differences in the way that the two types of cells are operated. This is most easily done by carrying out kinetic experiments to measure the recovery of material to the froth as a function of time. A useful model for flotation kinetics, which includes a term for both flotation rate and ultimate flotation recovery, is:

$$r = R\{1-[1-\exp(-Kt)]/Kt\}$$

where: r = total weight of component recovered at time t ,
 t = time,
 K = rate constant,

R = ultimate theoretical weight recovery at “infinite” time.

This model takes into account the fact that the hydrophobic particles vary in size and degree of hydrophobicity, and is therefore more appropriate than conventional reaction kinetics expressions that are intended to apply to systems of identical molecules. It is particularly useful for correlation of laboratory results with plant results. In conventional laboratory testwork, it is common for the parameter R to be the most important in determining the flotation performance, because laboratory tests are often run until all floatable material is recovered. In the plant, it is common for the parameter K to be most important, because it is too expensive to provide enough cell volume to recover all material that does not float in a short time. Because of this difference in operation, the results of laboratory studies can be very poor predictors of plant performance. To correct this, it is best to run timed-flotation laboratory tests which can produce kinetic data, so that the R and K performance can both be determined. Then, based on the residence time of the plant-scale units, it can be determined whether the plant performance is being dominated by kinetics (K) or by the ultimate recovery (R) (Klimpel, 1995).

1.7.2 Flotation Cell Selection

Flotation cells for use in a plant must be selected based on laboratory and pilot-scale data. Laboratory tests are usually carried out as batch experiments and are generally quite straightforward, although it is necessary to keep a few points in mind: (a) The pulp must be agitated sufficiently to keep all particles in suspension; (b) It is often necessary to condition the reagents with the minerals for a period of time to ensure good coverage with collector; (c) In many cases, adding frother in stages along with makeup water may be necessary to keep the pulp level and froth depth constant; (d) The capacity of the cell increases as the percent solids increases, and so the best process economics are achieved at the highest percent solids practical. The most important information from this testwork is:

- (1) Optimum grind size of the ore. This depends not only on the liberation characteristics of the ore, but also on floatability. Excessively coarse particles will be too large to be levitated by attached bubbles, and excessively fine particles will float poorly due to not striking the bubble surfaces, oxidation effects, or other problems. The coarsest material that can be floated is normally around 300 μm , while the finest particles are around 5 μm .
- (2) Quantity of reagents needed, and the appropriate points in the circuit to add each reagent.
- (3) Optimum pulp density. This is necessary for determining size and number of flotation cells for a given capacity.
- (4) Flotation time needed to reach desired recovery. It is important to be aware that a longer time is needed for flotation in the plant than in the laboratory, mainly due to the increased time needed

to move through the large equipment. Typical comparative flotation times for different minerals are shown in Table 2.

Table 2: Comparison of optimum flotation times in the laboratory and in the plant (Metso, 2006)

Material Floating	Flotation Times in Industrial Rougher Flotation Cells, Minutes	Usual Laboratory Flotation Times, Minutes
Barite	8 – 10	4 – 5
Coal	3 – 5	2 – 3
Copper	13 – 16	6 – 8
Effluents	6 – 12	4 – 5
Fluorspar	8 – 10	4 – 5
Feldspar	8 – 10	3 – 4
Lead	6 – 8	3 – 5
Molybdenum	14 – 20	6 – 7
Nickel	10 – 14	6 – 7
Oil	4 – 6	2 – 3
Phosphate	4 – 6	2 – 3
Potash	4 – 6	2 – 3
Sand (impurities floated)	7 – 9	3 – 4
Silica (from iron ore)	8 – 10	3 – 5
Silica (from phosphate)	4 – 6	2 – 3
Tungsten	8 – 12	5 – 6
Zinc	8 - 12	5 – 6

(5) Variability of the ore. Since ore properties vary from point to point in the mine, it is critical to run experiments not just with ore from one location, but from several locations.

(6) Corrosive and wear properties of the ore, which are needed for selecting appropriate materials of construction for the plant equipment.

(7) Type of circuit, number cells per bank, number of flotation stages, and appropriate locations for recirculation of intermediate products. The number of cells per bank depends on the flotation characteristics of the material being floated. Typical practice can be as low as 3 cells or as many as 17 cells per bank, as shown in Table 3.

Table 3: Normal numbers of cells per bank in froth flotation circuits (Metso, 2006).

Material Being Floated	Cells Per Bank								
	2	4	6	8	10	12	14	16	
Zinc				█	█				
Tungsten				█	█	█			
Silica (from phosphate)		█	█						
Silica (from iron ore)					▨	█	█		
Sand		▨	█	█					
Potash			█	█					
Phosphate		▨	█	█					
Oil			█	█					
Nickel						▨	█	█	
Molybdenum							▨	█	█
Lead			▨	█	█				
Fluorspar			▨	█	█				
Feldspar			▨	█	█				
Effluents			▨	█	█				
Copper							▨	█	█
Coal		▨	█	█					
Barite			▨	█	█				

Example Calculation:

Problem: As an example of sizing flotation cells, consider the following copper ore:

Specific gravity of dry ore = 2.7

Optimum Percent Solids in Laboratory Flotation Machine = 30%

Optimum Laboratory Flotation Retention Time = 6.5 minutes

Assume that the flotation facility will need to process 14,500 metric tons of dry ore per day.

Solution: First, from Table 2, we see that the average laboratory flotation time for copper is 7 minutes, and the average plant flotation time is 14.5 minutes. The scale-up factor is $14.5/7 = 2.07$, and so the time needed for flotation in the plant for this particular ore is $(6.5)(2.07) = 13.5$ minutes. A feedrate of 14,500 metric tons dry ore/day will require a flow of $(14,500/1440 \text{ min/day}) = 10.07$ metric tons/minute, and so for a 13.5 minute residence time there will need to be $(13.5)(10.07) = 136$ metric tons of ore retained in the flotation bank.

Since the slurry must be 30% solids, 136 dry tons of ore will equal $(136/0.3) = 453$ metric tons of slurry. Since the ore has a specific gravity of 2.7, the specific gravity of the slurry can be calculated from the relation $(100/\rho_{\text{slurry}}) = (X/\rho_{\text{solids}}) + ((100-X)/\rho_{\text{water}})$, where X is the percent solids, and ρ_{slurry} , ρ_{solids} , and ρ_{water} are the specific gravities of the slurry, solids, and water, respectively. We therefore have $(100/\rho_{\text{slurry}}) = (30/2.7) + (70/1.0)$, and solving for ρ_{slurry} we find

that the specific gravity of the slurry is 1.23. The total volume of the 453 tons of slurry that the cells must hold will be $(453 \text{ metric tons})/1.23 = 368$ cubic meters. However, when the pulp is aerated it will consist of approximately 15% air and 85% slurry by volume, so the actual volume of pulp needed will be $368/(0.85) = 433$ cubic meters.

Cells of 14.15 cubic meters (500 cubic feet) are a standard size, and so if these are used we will need $433/14.15 = 30.6$ cells, or approximately 31 cells. Referring to Table 3, we see that for copper we should use between 12 and 17 cells per bank, with 14 to 17 cells being optimum. Two banks of 16 cells would give 32 total cells, which would provide the 31 cells needed with some extra capacity. The cells would then be arranged in the individual banks as per the manufacturer's recommendations.

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