CHAPTER 7.5

Flotation Chemicals and Chemistry

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Successful practical mineral recovery by flotation requires careful manipulation and control of mineral surface and aquatic chemistry via flotation chemicals with concomitant attention paid to physical-mechanical and operational aspects of the integrated system. This chapter is a concise compilation and analysis of the vast, but somewhat fragmented, body of knowledge pertaining to flotation chemicals used to control mineral surface and aquatic chemistry, presenting guidelines that can be used to fulfill practical mineral flotation requirements. It is written for the flotation practitioner—novice to expert, including students and aspiring young professionals.

A considerable effort has been made to bring all the bits and pieces of information scattered in the published literature and in industrial practice into one complete compilation. This is particularly germane after a century of flotation practice and serves to (1) highlight and fill some of the knowledge gaps; (2) rectify misconceptions, misrepresentation, and myths; (3) and provide practical guidelines. Such a complete compilation is not readily available in the literature.

The historical and theoretical aspects, which are well documented in the literature, are highlighted here only when necessary to support the applied aspects of flotation chemicals and chemistry, reagent selection, evaluation, and optimization with major emphasis on relevance to operator needs and plant practice. Pitfalls and gaps arising from somewhat arbitrary and reductionist practice in reagent applications are identified, and the impact of environmental regulations on current and future reagent development is discussed. The importance of frothers and modifiers, which in the past has received less overall attention than collectors, is highlighted. The critical need for a rational, holistic ("total system") approach for reagent design, selection, and optimization is discussed with a view to provide remedies against pitfalls, thereby allowing development of robust reagent schemes.

Reagent selection for any given application is strongly dictated by the surface characteristics of minerals in the ore pulp and the particular set of chemical, physical-mechanical, and operational conditions that exist in the plant (reagent choice is not predictable based on surface properties of single minerals determined in simple model systems using a single reagent). Since one does not have real-time information on the in situ mineral surface compositions, mineralogy, and properties of minerals in the pulp or sufficiently sophisticated models that could incorporate such information, one must rely on (i) empirical ore flotation testing, (ii) information on bulk mineralogy and liberation, (iii) a holistic application of fundamental concepts and insights in reagent–mineral interactions and mineral aquatic chemistry generated over many decades, and (iv) experiential knowledge to screen, evaluate, and select reagents. The complexity of natural ore systems invariably requires more than one collector, modifier, or frother to achieve metallurgical performance targets (recovery, grade, economics, environmental, etc.).

A chronology of innovations and major periods of development of flotation chemicals are given in Nagaraj and Farinato 2013 and 2016 (Table 1 therein). The practitioner can learn more from several older publications (Fuerstenau 1962; Somasundaran and Moudgil 1987; Malhotra and Riggs 1986; Mulukutla 1994; Nagaraj and Ravishankar 2007).

TERMINOLOGY AND CLASSIFICATION

As is typical of any technology that has evolved over a long period of time, terminology in flotation is rather loose, somewhat arbitrary, and often highlights merely one function or property, among many, of the reagents in question. There is also considerable discrepancy in the terminology and classification used between industry and academe; this is perhaps a reflection of differences in point of view between practitioners and academicians. The purpose of this section is to describe the terminology (and classification) adopted in this chapter and at the same time to identify a common ground that is meaningful to both research and practice.

Classification of Flotation Chemicals

The term *flotation agent* is sometimes used to describe flotation chemicals or flotation reagents, but its usage is discouraged;

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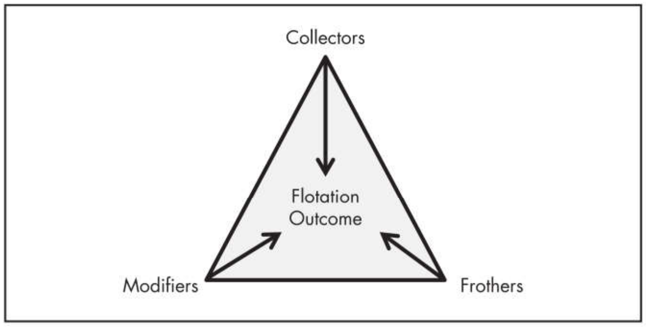
the terms *flotation chemicals* or *flotation reagents* are more meaningful and accurate and are, therefore, preferred (see Holman 1930). *Chemicals* and *reagents* are used interchangeably in the industry, and thus this chapter follows this common usage. Throughout the chapter, *flotation reagent* refers to any of the three classes of reagents—collectors, frothers, or modifiers used in flotation (Leja 1982). As depicted in the flotation reagent triangle in Figure 1, each of these three classes of reagents is important for achieving successful mineral separation.

Deliberately added modifiers (sometimes referred to as modifying agents) are a broad category of compounds that include any chemicals that cannot be classified as a collector or frother; examples include depressants, dispersants, pH regulators, activators, gangue-control reagents, and slime binding reagents, to name a few. Collectors, frothers, and modifiers are of equally critical importance and they undergo complex interactions with each other and the various minerals in the pulp. There is a trade-off in terms of mineral recovery and selectivity depending on mineralogy and plant conditions (Nagaraj 2005). Table 1 shows examples of the function provided by each class of reagent. No matter how the flotation reagents are categorized, however, the ultimate goal is to choose the appropriate combination of chemicals that will most economically and selectively separate the desired mineral species with high recovery.

In the academic (research) community, collectors, for example, are variously classified into ionic (cationic and anionic) and nonionic surfactants, sulfhydryl, thio, thiol, non-thio, non-thiol, soluble, insoluble, oily, hydrolysable, ionizable, and so forth (Leja 1982; Rao 2004). In the case of sulfide minerals, these classifications are inadequate because many diverse collector families are used, collector adsorption is predominantly through surface chemical reactions (chemisorption and surface precipitation), and electrostatic effects are not very relevant. In the industry, collectors are invariably referred to and selected by their chemistry (e.g., dithiophosphates, thionocarbamates, and the associated chain lengths of hydrocarbon substituents), which immediately suggests a link between performance and a particular combination of functional group and substituents. In other words, collectors are not selected in practice based on the above-mentioned academic classifications, but more on their functionality. Thus, a classification by functional group and substituents is more appropriate and scientifically meaningful in both research and practice. Similarly in non-sulfide flotation, a classification based on functional group is very useful and revealing in terms of performance characteristics.

A functional group is a well-defined specific group of atoms containing important electron donor atoms (S, N, O), in a molecule with distinct chemical properties independent of other atoms in the molecule attached to the group. For example, —OH in alcohols, —C(=O)OH in fatty acids, —OC(=S)S in xanthate, and so on. The term *functional group* is used widely to characterize the chemistry of small organic, oligomeric, and polymeric molecules. However, in a broader sense, the term can be applied to characterize many inorganic compounds as well—for example, PO_4^{3-} in sodium phosphate or in apatite mineral or CO_3^{2-} in sodium carbonate or carbonate minerals. The functional group is sometimes referred to as a ligand. Sometimes the whole molecule carrying a particular functional group is referred to as a ligand. The term *ligand* is more commonly used in coordination chemistry. In this chapter, ligand is often used to refer to either a collector or



Source: Nagaraj 2005

Figure 1 Flotation reagent triangle

Table 1 Classification of reagents*

Reagent	Functional Category or Attribute	Practical Classification (in industry)	Research Classification (in academe)
Collectors	Sulfide collectors	Xanthate, dithiophosphate, thionocarbamate	Nonionic, anionic, cationic, hydrolysable, ionizable, soluble, insoluble, surfactants
	Non-sulfide collectors	Carboxylates, sulfonates, amines, hydroxamates	
Frothers	Froth stability, froth mobility, carrying capacity	Aliphatic alcohols, polyglycols	Surfactants, foamability, foam stability
Modifiers	pH and E_p† modifiers, activators, depressants, dispersants, slime or fines control reagents, coagulation, flocculation, metal hydroxy species formation and adsorption control, froth control	Acids (sulfuric), bases (NaOH [sodium hydroxide], lime, soda ash), redox reagents (NaSH [sodium hydrosulfide], Na_2S [sodium sulfide], Nokes), metal salts (Cu^{2+}), depressants and dispersants (silicate, phosphate, carboxylate, carbonate, sulfonates, polysaccharides), complexing reagents (cyanide, sulfite, sulfoxy species [S_xO_y]), alcohols, coagulants (high-charge metal ions, low-molecular-weight polymers), and flocculants (high-molecular-weight polymers) and many others	Reagents to control pH and E_h†; depressants, complexing reagents, dispersants, activators, flocculants, coagulants, surface charge density

*Although individual classification is given for collectors, frothers, and modifiers, formulations (blends) are used frequently for collectors and frothers (and sometimes modifiers) in industry, given the complex and routinely changing mineralogy/ore types in the plant and the wide size distribution of mineral particles that have to be treated without significant recovery losses in the coarse or fine size ranges and in concentrate grades.

†Ep is pulp potential, most often with respect to an Ag/AgCl reference electrode. E_h is solution or pulp potential with reference to a standard hydrogen electrode.

a functional group capable of forming metal complexes (via covalent or coordinate-covalent bonds).

The term *oily collectors* is used in several contexts, which can be confusing, because there is a distinction in the manner of their interaction with mineral surfaces. A useful categorization is based on whether or not there is an active functional group involved in adsorbing to a mineral surface. For example, thionocarbamates, thioureas, and xanthate esters all contain active sulfur functionalities involved in chemisorption to sulfide mineral surfaces. They are considered as oily collectors because they have very marginal solubility in water and carry no charge under typical use conditions, although they may ionize at extreme values of pH depending on their pK_a. Hydrocarbon oils (e.g., petroleum-based—mainly nonpolar; Seitz and Kawatra 1986), on the other hand, are also referred to as oily collectors (or extenders). Such chemicals, which are used in great quantities in sulfide and non-sulfide ore flotation, have very low solubility, do not contain active electron donor atoms (i.e., S, N, O), and work in a support fashion by co-adsorbing to mineral surfaces that are naturally hydrophobic (e.g., molybdenite) or have been made hydrophobic by the primary collector (e.g., fatty-acid-treated apatite; xanthate-treated sulfide minerals). Extenders in droplet form can act as a locus around which hydrophobic mineral particles can cluster, thereby improving collision efficiency with air bubbles; these clusters can also include air bubbles. Extenders co-adsorbed onto collector-coated particles can increase the effective area of the hydrophobic domain. Non-functionalized oils are also commonly used in froth modification and control.

Frothers are grouped into soluble and partially (or sparingly) soluble frothers (Booth and Freyberger 1962). The soluble frothers are polyglycols and their alkyl ethers. Partially soluble or sparingly soluble frothers comprise aliphatic and aromatic alcohols, terpineols, aliphatic aldehydes, ketones, and esters. In the industry, frothers are commonly referred to and selected by their chemistry, namely, alcohols and glycols and their mixtures; solubility is implicit when the chemistry is specified. Other classifications or selection criteria are being actively explored, for example, those based on hydrophilic-lipophilic balance, critical coalescence concentration, or by flotation kinetics and stability. However, these are not fully developed at this stage. Given that $-OH$ is the most important functional group (other functional groups constitute a small part of the total frother usage in the industry), classification based on solubility differences is also quite acceptable. Although molecular weight (MW) and branching play a role, they can also be linked to solubility. In non-sulfide flotation, though a separate frother is not universally used, long-chain surfactants with a variety of functional groups and short-chain alcohols and glycols are sometimes used as froth modifiers. Even in these systems, a classification by functional group is meaningful.

The terminology used for modifiers is more contentious. Modifiers essentially enhance the activity and/or selectivity of collectors and frothers, and overall separation efficiency and selectivity. There is no single, generally accepted classification of modifiers. They are variously referred to as pH modifiers (or regulators), depressants, dispersants, flocculants, coagulants, activators, deactivators, promoters, froth modifiers, viscosity modifiers, and slime-blinding reagents. Often the terms *depressants* and *dispersants* are used interchangeably.

The term *promoter* has occasionally been mentioned in the literature to refer to certain modifiers; however, there is no category of modifier that should be referred to as a "promoter." *Promoter* usually refers to a chemical that is more appropriately termed a *collector*, but such usage is far less common. It is best to avoid the use of the term *promoter* altogether.

Slime-blinding reagents refer to chemicals such as dextrin or guar that adsorb onto fine particles (clays, amorphous carbon, etc.) and "blind" them to prevent these fine particles from interfering with flotation of value minerals.

The term *dispersant* has different connotations in sulfide and non-sulfide systems. It is used loosely in sulfide flotation systems where its primary function appears to be one of controlling slimes (i.e., to prevent them from interfering with recovery or grade of value mineral species) and pulp viscosity and not for providing colloidal stability to suspensions. In non-sulfide systems, a dispersant's multiple functions are widely exploited (e.g., to prevent aggregation to moderate pulp viscosity during conditioning, and/or improve selectivity of collector adsorption by preventing collector adsorption on unwanted mineral sites).

The term *modifier* is sometimes used in a very narrow sense to represent a specific function among many (e.g., a pH modifier). All such classification or categorization fails to recognize that in the complex flotation system, a single modifier invariably has multiple functions, which vary in number and intensity from system to system. However, it is difficult to establish a distinct classification that comprises the entire spectrum of applications. The best recommendation is to use the term *modifier* (distinct from *collectors* and *frothers*) in a broad sense and to recognize that it constitutes the third apex of the flotation reagent triangle (Figure 1) and it has important implications in flotation research and practice.

Qualitative descriptors are used routinely in research and practice to indicate reagent performance (e.g., use of the terms *strength* and *selectivity*). These are relative terms, though they are sometimes used as if they were absolute. They are used interchangeably to refer to strength or selectivity of adsorption of a reagent (thermodynamic or kinetic) on individual minerals or of flotation recovery of a value mineral at a given dosage or under a given set of plant conditions. Thus, descriptors such as "strong or weak collector (modifier, frother)" or "selective collector (modifier, frother)" are necessarily qualitative; implicit in the description is that some reference is used. Similarly, qualitative descriptors are routinely used for frothers (e.g., watery froth or dry froth). These terms will be used as such in this chapter, for they serve a useful purpose in plant practice in the absence of quantitative descriptors.

Ultimately, what matters the most in terms of plant practice is whether the selected reagents from the flotation reagent triangle are able to meet the selectivity and recovery targets in the plant for the desired value mineral species in the most economical manner.

Classification of Ores: Sulfides and Non-Sulfides

In the field of mineral processing, ores and minerals have been classified in many ways: metallic or nonmetallic; ferrous or nonferrous; industrial minerals; construction minerals; soluble or semi-soluble or salt-type; oxide ores; silicate ores; carbonate ores; base metal sulfide ores; precious metals ores; and so on. The myriad classifications are partly historical and partly based on differences in perspectives arising from different mineral industry segments, the academic community, ore/mineral product properties, their end use, and the particular value mineral/metal contained in the ores.

Whereas for sulfide minerals the classification is usually based on the dominant metallic element(s), for non-sulfide minerals the classification has been based on any of a variety of attributes, including crystal structure, solubility in water, or other physical properties such as metallic or nonmetallic character, and ferrous versus nonferrous and industrial uses. This leads to overlapping and possibly confusing categories in which one might misplace non-sulfide minerals. It would appear that there is really no need for any type of classification other than the distinction from sulfide minerals when one considers the types of collectors, modifiers, processing schemes, strategies, and equipment used in the industry for the flotation separation of all these types of non-sulfide minerals. Indeed in plant practice, the decisions on flow sheets and reagent schemes are not based on whether the ore is salt type or oxide or industrial mineral, and so forth. The various physical properties of non-sulfide minerals, and the mineralogical associations, merely suggest the conditions that might be useful in flotation separations. For example, both sylvite (KCl) and quartz (SiO_2) can be floated by the same amine at approximately the same pH, yet these minerals have very little in common. The most significant factor, which dictates the choice of a separation scheme, is that there are only small differences in surface properties between a value mineral and the gangue, both of which are non-sulfide minerals. Highly specific treatment conditions are frequently required to achieve adequate selectivity and satisfactory metallurgy, the most critical aspect of which is generally the quality and purity of the finished product.

Thus, in discussing the chemistry and application of flotation reagents, none of the mineral classification schemes noted previously are adequate or enlightening (or useful). Nagaraj (1987) provided arguments for a convenient and useful classification based on the predominant occurrence and source of elements in earth resources. *Thus from the perspective of flotation reagents, minerals/ores are classified into two distinct groups: sulfide minerals/ores, and non-sulfide minerals/ores.* The rationale/basis for this classification is found in Nagaraj and Ravishankar (2007).

CHEMICALS USED IN SULFIDE AND NON-SULFIDE FLOTATION—BASIC CONCEPTS AND REAGENT FUNDAMENTALS

Interfacial chemistry is at the heart of flotation separations. Interfacial chemistry can be modulated and controlled with the use of a wide variety of chemicals. These chemicals and the minerals in the ore participate in a wide range of chemical processes in the pulp and froth zones. That is, these processes occur both at the mineral–solution and air–solution interfaces as well as in the bulk aqueous phase. All these processes together constitute *mineral (or ore) aquatic chemistry*. Interfacial processes include hydration, dissolution, hydrolysis, reduction–oxidation (redox) reactions, adsorption (chemisorption, physisorption), surface reactions, and surface precipitation. These processes occur even in the absence of any deliberately added flotation chemicals. Bulk aqueous processes include hydrolysis, redox processes, complexation (Lewis acid–base interactions), and precipitation. All these processes must be considered together because they occur simultaneously (though at different rates). When chemicals are added, many of the interfacial and bulk aqueous phase processes are immediately altered via many pathways, and the added chemicals become a part of the system. The complexity increases substantially; however, many of the processes (or pathways) may become unimportant or even shut down. For example, addition of a collector may reduce solubility of a mineral on which it adsorbs, or passivate the mineral and thus shut down redox processes. Addition of lime may have similar effects. Ore aquatic chemistry begins when the ore is first exposed to the aqueous phase. An understanding of the basic concepts in ore aquatic chemistry is critical for the design, selection, and optimization of flotation reagents and for plant problem-solving. There is extensive literature (though fragmented) on ore or mineral aquatic chemistry. The topic of ore aquatic chemistry is very broad and beyond the scope of this chapter.

Although fundamental studies focus invariably on relatively pure, single reagents (justifiably so), in plant practice, invariably, combinations of reagents and single minerals (such as formulations of collectors or frothers) are used, and ores have multiple mineral phases often associated with each other. This creates numerous competitive processes in practical ore systems, which are absent in the simplified systems used for fundamental studies. Indeed, commercial-grade reagents are rarely pure reagents (i.e., they may have more than one active component as a result of the manufacturing process, or they may have impurities, which may influence reagent performance). Some of the frothers may be deliberate formulations of several raw materials (which may be a by-product or waste stream from a manufacturing process), which themselves may be mixtures. Thus, results of fundamental studies based on single-mineral, single pure-reagent systems are often difficult to translate to practical systems.

Mineral processing via flotation consists of a series of unit operations whose main physical success metric is metallurgical outcome (e.g., recovery and grade). The concepts and factors relevant to the chain of events leading to successful flotation are shown schematically in Figure 2. This provides context for understanding the parameters that can affect flotation performance and the factors that should be taken into account to optimize a chemical treatment program.

Successful separation via flotation is based on leveraging wettability differences of mineral particle surfaces in a mixture so that the more hydrophobic particle surfaces have a greater probability of attaching to bubbles, thereby selectively transporting them into the froth zone. Not only must the surfaces of the mineral particles to be floated be made hydrophobic, the surfaces of all the rest of the mineral particles must be maintained in a hydrophilic state. Thus *interfacial chemistry is at the heart of flotation*. The components of an effective flotation reagent package (collectors and modifiers), which are the principal means by which interfacial chemistry is affected, must operate in and take advantage of the environment of the pulp phase (water chemistry, pH, E_p, etc.). This allows maximizing the wettability difference between particles to be floated and gangue mineral particles.

FLOTATION REAGENTS—PLANT PRACTICE

Reagent design and selection for a given flotation separation is inevitably a compromise that must take into account not

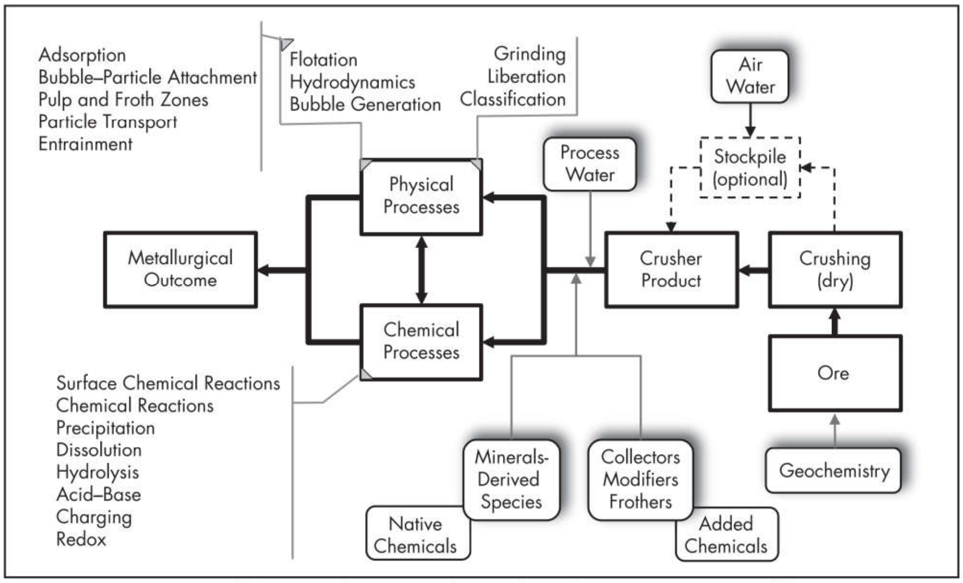


Figure 2 Concepts and factors relevant to chemical performance in mineral flotation

only the primary function of a reagent (e.g., collector, frother, or modifier) but any secondary functions (intended or inadvertent) and potential interactions with other components in the flotation cell (dissolved species, frother–collector interactions, etc.). As discussed in the previous section, most plants use combinations of collectors to solve their problems. This applies to modifiers and frothers as well.

Major factors that can affect reagent design and selection include mineralogy, toxicity, environmental impact, cost–performance, physical and chemical stability, ease of manufacture, raw material cost and availability, and performance attributes (e.g., strength, selectivity, froth properties, and breadth of applicability). Chemicals made from variable raw material feedstocks (e.g., animal or vegetable origin) tend to have a much greater variability in composition distribution than those made via synthetic or mineral-sourced feedstocks (petroleum-derived alcohols, soda ash, sulfuric acid from pyrite, etc.). Since flotation reagents for non-sulfide mineral recovery more typically fall in the first class (e.g., fatty acids, amines, petroleum sulfonates), more variability is encountered in product quality and therefore performance. Consequently, reagent selection is more dependent on the manufacturing process and raw material source. Impurities in the manufactured products may influence regulatory aspects and environmental impact. For naturally derived products, many of the regulations are grandfathered. Other custom-made reagents typically have tighter specifications for active components and impurities, making reagent selection less dependent on manufacturing process or raw material source. Reagents typically used in sulfide flotation fall into this second class, requiring no further discussion of raw material sources or manufacturing processes.

Many of these factors are not amenable to quantification, making it difficult to develop specific guidelines for use. Under such circumstances, one must resort to efficient empirical exploration of reagent combinations, doses, and operational conditions to arrive at optimized schemes (see the "Reagent Selection and Optimization" section later in this chapter).

Reagents for Base Metal Sulfides and Precious Metals

Classification

Sulfide ore flotation can be divided into the following four metal-value-based groups based on certain common features of ores and mineralogy in each group, flow sheets, and metallurgical objectives:

1. Cu, Cu-Mo, Cu-Co, and Cu-Au ores
2. Complex, polymetallic ores such as Pb-Cu-Zn-Au-Ag
3. Primary Au and platinum group metal (PGM) ores
4. Ni and Ni-Cu ores

Other minor, value elements (tellurium, rhenium, bismuth, antimony, cobalt, etc.) may be recovered from these ores, but these are invariably by-products that may or may not be economically feasible or sensible to recover. In groups 1 and 2, separation of sulfides from each other is necessary (Cu sulfides from pyrite, Cu sulfides from galena, etc.) in addition to separations of sulfides from non-sulfides, and selective reagents are invariably used judiciously. In group 3, the objective is to recover all recoverable value sulfides and precious metals at as high a grade as possible (lowest mass recovery), and strong collectors are used for this purpose. In group 4, both selective flotation and bulk flotation are practiced depending on the ore type (e.g., in massive sulfide ores, selective separation is required; in mafic and ultramafic ores, bulk flotation is practiced). There are significant differences in flow sheets, operating strategies, and operating philosophies among these groups. There are also differences in the particular reagent choices and their usage or application. In spite of this division and the differences, all four groups also have much in common, especially reagent chemistry (e.g., the same families of collectors used in all groups) and mechanisms of interaction with minerals (e.g., dominated by chemisorption and electrochemical processes), which is not surprising given that the important value minerals in these ores are based on metals that are all grouped together in the periodic table and exhibit similar chemical properties.

Collectors

It is well established that the main function of the collector is to impart sufficient hydrophobicity (i.e., reduced water wettability) to the mineral surface so that the probability of bubble–mineral attachment is increased and the probability of detachment is decreased. It is also well established that a collector molecule accomplishes this function by adsorbing on the mineral surface. A separate "collector" is not always necessary; a mineral can be floated without a collector if it is naturally hydrophobic (e.g., molybdenite) or made hydrophobic as a result of interfacial processes (e.g., chalcopyrite after mild oxidation resulting in a metal-deficient, sulfur-rich hydrophobic surface leading to collectorless flotation). Sometimes a modifier can remove hydrophilic coatings on a mineral, thus exposing a hydrophobic surface. However, in plant practice, a collector is almost always necessary to ensure maximum flotation rate and recovery of values or rejection of gangue; no plant relies on natural or induced hydrophobicity of one specific mineral. However, collector adsorption and the consequent development of hydrophobicity on the mineral surface do not guarantee the desired flotation outcome, since flotation is a probabilistic physicochemical process. Flotation is a delicate balance between buoyancy and gravitational forces; any perturbation (chemical, physical, or operational) can tip the balance. Flotation outcome cannot be predicted exactly, but probabilities of the various subprocesses can be estimated, some better than others. Collector, modifier, and frother work in concert. It is also necessary for the collector to *not* alter the wettability of the gangue minerals to provide adequate selectivity in the separation process. Collector adsorption onto gangue minerals (unless a reverse flotation process is in effect) may have to be actively suppressed through a judicious use of modifiers to achieve the best separation.

A perusal of flotation literature on chemical aspects over the past 100 years would indicate that collectors have been accorded paramount importance and more attention compared to modifiers and frothers. However, viewed from the perspective of a flotation plant's overall goals of maximizing recovery, grade, and profitability, such singular focus on collectors is extremely unbalanced. Although collectors do play a critical role in providing a part of the solution, their performance is intimately affected by the correct choice of modifiers and frothers. This is particularly important in non-sulfide mineral flotation. In other words, collectors are necessary but not sufficient to control a flotation operation. The poor availability of concise information on modifiers and frothers is an area for improvement. See the "Modifiers" section later in this chapter for general guidelines.

Currently used and recently developed collectors for separation of metal sulfides and precious metals are shown in Table 2. Additional details can be found in manufacturer's handbooks (e.g., *Mining Chemicals Handbook* [Cytec Industries 2010]). General guidelines for various ore types are provided later in this chapter.

Xanthates continue to account for the largest consumption of collectors in terms of volume used in sulfide mineral flotation, but not necessarily in terms of total value of the minerals recovered. Large quantities (or dosages) of xanthates are used for bulk flotation of all the sulfide minerals and precious metals in primary Au, PGMs, and certain Ni ores without regard for selectivity between floated species (selectivity against gangue is presumed). Even in these cases, other more selective collectors are also required to augment performance deficiencies of xanthates and maximize recovery of values. Where selectivity between sulfides is the key goal (as in Cu, Cu-Mo, Cu-Co, Cu-Au, Ni-Cu, complex sulfides, and polymetallic ores—all of which make up the bulk of sulfide flotation), xanthate is not the primary collector; other more selective collectors such as dithiophosphinates, thionocarbamates, and dithiophosphates serve as the primary collectors, with xanthate used as an auxiliary (or secondary) reagent. In fact, the use of specialty collectors has grown significantly over the past four decades, most significantly during the past two decades, in part due to the prevalence of difficult-to-process ores with complex mineralogy and the desire for safer, greener flotation reagents.

Those acquainted with plant practices would realize that a single collector cannot be universally effective for the large mineralogical diversity encountered in commercial flotation operations. Flotation practitioners have realized this fact and have adopted reagent combinations in response to the separation challenges faced in the plant.

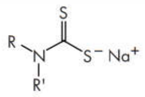
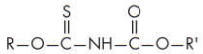
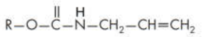
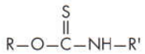
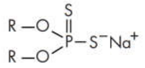
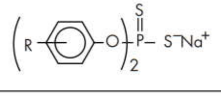
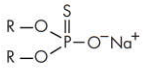
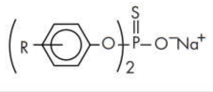
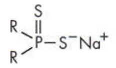
Hydrocarbon oils are widely used as collectors for molybdenite, extenders for other primary collectors (to enhance particle hydrophobicity, particle-bubble-oil cluster formation, improved coarse particle recovery) and for froth modification and control to improve selectivity. Extenders play a role in froth modification and control. Hydrocarbon oils can produce a highly mineralized froth that drains more easily, thereby reducing entrainment of fine hydrophilic gangue and improving selectivity. Over-frothing due to the presence of slimes can be reduced or eliminated using these oils (Seitz and Kawatra 1986).

Significant advances have been made in the past three decades in reagent design, selection, and systematic structure–activity relationships. These are described in several notable articles and books (Jones and Oblatt 1984; Aplan and Chander 1987; Somasundaran and Moudgil 1987; Nagaraj et al. 1989; Pradip and Fuerstenau 1991; Mulukutla 1994; Nagaraj 1997; Pradip et al. 2002a, 2002b; Herrera-Urbina 2003; Nagaraj and Ravishankar 2007).

Frothers and Frothing

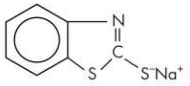
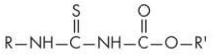
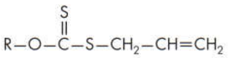
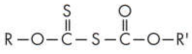
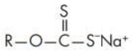
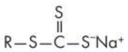
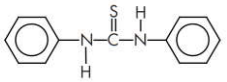
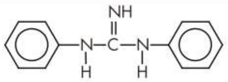
Frothers and the froth zone (also called the "froth phase") play a critical role in flotation, which will ultimately be judged based on the recovery of values and the grade of the flotation concentrate obtained for each ore type. Frothers aid in froth formation and in achieving the desirable (or optimum) characteristics of the froth to facilitate selective separation and transport of targeted particles. They reduce bubble size by reducing bubble coalescence in the pulp zone, which can affect water and solid transport into the froth zone. Frothers can also contribute to the transient stability of thin liquid films in the froth zone, thereby impacting bubble coalescence rates, water holdup, froth mobility, and carrying capacity. For example, all else being the same, a polyglycol frother usually results in a wetter froth than does methyl isobutyl carbinol (MIBC). Careful selection of the most appropriate frother, combined with practical application expertise, is essential for maximizing mineral separation. In the froth flotation process, as practiced in most operations using mechanical cells, columns, and even the emerging new designs (e.g., the Woodgrove devices;

Table 2 Collectors used in sulfide mineral flotation

No.	Chemical Class	Typical Compounds Used	Structure	Manufacture	Product Form and Aqueous Solubility	Plant Application	Hydrolytic Stability*	Resistance to Aqueous Oxidation*
1	Thiocarbamic acids (dithio derivatives)	Dithiocarbamate, dialkyl, sodium (R = R' = ethyl or butyl)		Reaction of dialkyl amines with carbon disulfide	Aqueous solutions of sodium salts	Limited use in PGMs; primary Au, Cu, and polymetallic ores	High	Medium
2	Thiocarbamic acids (thiono derivatives)	Thionocarbamate, alkoxycarbonyl alkyl (R' = ethyl or butyl; R = C_2, C_3, C_4 etc.). Note: Product where R' = ethyl has known toxicity†	 $R-O-\overset{S}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-O-R'$	Reaction of isothiocyanate with alcohol	Oily; insoluble in water, but disperse well in water	Widely used for Cu, Cu-Mo, Cu-Au, and Cu-Co ores in a wide pH range (4-11); very selective against gangue iron sulfides	Medium	High
3	Thiocarbamic acids (allyl thiono derivatives)	Thionocarbamate, allyl alkyl (R = butyl)	 $R-O-\overset{\|}{C}-\overset{H}{N}-CH_2-CH=CH_2$	Reaction of allyl isothiocyanate with alcohol	Oily; insoluble in water, but disperse well in water	Widely used in Cu, Cu-Mo, Cu-Au, Zn, and Cu slag circuits; stronger than corresponding dialkyl thionocarbamates	High	High
4	Thiocarbamic acids (dialkyl thiono derivatives)	Thionocarbamate, dialkyl (R = isopropyl or butyl; R' = methyl or ethyl)	 $R-O-\overset{S}{\overset{\|}{C}}-NH-R'$	Reaction of alkyl xanthate with ethyl amine using catalyst	Oily; insoluble in water, but disperse well in water	Widely used for Cu, Cu-Mo ores; very selective for copper sulfides; selective against gangue sulfides	High	High
5	Thiophosphoric acid (dialkyl derivatives)	Dithiophosphate, dialkyl, sodium (R = ethyl, isopropyl, isobutyl, or isoamyl)		Reaction of alcohols with phosphorous pentasulfide	Aqueous solutions of sodium salts	Very widely used, next to xanthate; more selective than xanthate; used as primary or secondary collectors; general purpose collector for most sulfides and precious metals ores	High (at high pH)	Medium
6	Thiophosphoric acid (diaryl derivatives)	Dithiophosphate, dicresyl, sodium or ammonium, or in the acid form (R = methyl)		Reaction of cresols with phosphorous pentasulfide	Aqueous solutions of sodium and ammonium salts	Mostly for complex and polymetallic sulfide ores (Pb-Ag-Zn-Cu); sporadic use in Cu, Cu-Mo-Au ores	High (at high pH)	Medium
7	Thiophosphoric acid (dialkyl monothio derivative)	Monothiophosphate dialkyl, sodium (R = ethyl or isobutyl)		First hydrolysis of the corresponding dithiophosphoric acids	Aqueous solutions of sodium salts	Mostly for Cu-Au and Au ores; excellent collectors in acid circuits; selective precious metal flotation in alkaline circuits	High	High
8	Thiophosphoric acid (diaryl monothio derivatives)	Monothiophosphate dicresyl, sodium (R = methyl)		First hydrolysis of the corresponding dithiophosphoric acids	Aqueous solutions of sodium salts	Mostly for Cu-Au and Au ores; excellent collectors in acid circuits; selective precious metal flotation in alkaline circuits	High	High
9	Thiophosphinic acid	Dithiophosphinate, dialkyl, sodium (R = isobutyl)		Phosphine reacted with alkene and sulfur	Aqueous solutions of sodium salts	Widely used for complex and polymetallic (Pb-Ag-Zn-Cu), Cu-Mo-Au, Au, and Cu-Ni ores; very selective against gangue sulfides; rapid flotation kinetics; low dosages	High	High

(continues)

Table 2 Collectors used in sulfide mineral flotation (continued)

No.	Chemical Class	Typical Compounds Used	Structure	Manufacture	Product Form and Aqueous Solubility	Plant Application	Hydrolytic Stability*	Resistance to Aqueous Oxidation*
10	Thiol	Mercaptan, alkyl (R = dodecyl)	R—SH	Reaction of alcohol with H_2S	Oily; insoluble in water	Very limited use as a smaller component of formulations	High	Low
11	Thiazole	Mercaptobenzothiazole		Reaction of aniline, carbon disulfide and sulfur under high pressure	Aqueous solutions of sodium salts	Mostly for complex sulfide, polymetallic, and Au ores, tarnished sulfides, and as auxiliary collectors	High	Medium
12	Thioethers	Sulfide, dialkyl (R = octyl and R' = ethyl)	R—S—R'		Oily; insoluble in water	Very limited use; often as a minor component in formulations	High	High
13	Thiourea	Thiourea, alcoxycarbonyl alkyl (R = C_2, C_3, C_4 etc.), R' = butyl or ethyl product where R' = ethyl has known toxicity	 $R{-}NH{-}\overset{\overset{S}{\|}}{C}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'$	Reaction of isothiocyanate with amine	Oily; insoluble in water, but disperse well in water	Similar to alkoxycarbonyl thionocarbamates, but with a few unique properties	High	High
14	Thioester (dithio derivatives)	Xanthate ester, *allyl* alkyl (R = amyl)	 $R{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}CH_2{-}CH{=}CH_2$	Reaction of alkyl xanthate with allyl chloride	Oily; insoluble in water, but disperse well in water	Widely used for Cu, Cu-Mo, Cu-Au, and Au ores; very selective for copper sulfides and precious metals; excellent for molybdenite	Medium	High
15	Thioester (dithio derivatives)	Xanthogen formate, dialkyl (R' = ethyl; R = ethyl, isopropyl or isobutyl)	 $R{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'$	Reaction of xanthates with alkyl chloroformate	Oily; insoluble in water, but disperse well in water	Very limited use; mostly for Cu, Cu-Mo; known to be acid circuit collectors	Low	Medium
16	Thiocarbonic acid (dithio derivatives)	Xanthate, alkyl (R = ethyl, isopropyl, n-butyl, isobutyl, amyl)	 $R{-}O{-}\overset{\overset{S}{\|}}{C}{-}S^{-}Na^{+}$	Reaction of alcohols with carbon disulfide	Solid form of sodium or potassium salts. High solubility in water. ~30% solutions are sold when practical.	Generic (nonselective) collectors for all sulfide ores; alloys and minerals carrying Au, Ag, PGMs; sulfidized oxide minerals of Cu, Pb, and Zn; primary collectors for Ni, Au, and PGM ores; secondary collectors for all other ores	Low	Low
17	Thiocarbonic acid (trithio derivatives)	Trithiocarbonate, alkyl, sodium salt (R = butyl)	 $R{-}S{-}\overset{\overset{S}{\|}}{C}{-}S^{-}Na^{+}$	Reaction of mercaptan with carbon disulfide	Aqueous solutions of sodium salts	Very limited use (stench); general purpose collector	Low	Low
18	Thiourea	Diphenyl thiourea (thiocarbanilide)		Reaction of aniline, carbon disulfide and sulfur	Solid; insoluble in water	Very limited use (complex sulfides); used only as a small component in a formulation	High	High
19	Guanidine	Diphenyl guanidine		Reaction of cyanogen chloride with aniline	Solid; insoluble in water	Used for Cu-Ni matte separation in one plant	High	High
20	Hydrocarbon oils	Kerosene, diesel, burner oil, gas oil, fuel oil, pump oil, vapor oil, aromatic oils, vegetable and mineral oils	Complex mixtures of aliphatic and aromatic hydrocarbons, linear and branched.	Products of petroleum cracking and refining and natural oils	Liquids, oily; insoluble in water	Naturally hydrophobic minerals (MoS_2 [molybdenite], talc, sulfur, stibnite, graphite, and other forms of carbon); extender for other collectors; froth control	No hydrolysis except for vegetable oils	High

Adapted from Nagaraj and Ravishankar 2007

*Qualitative/relative ranking only.

†Residual ethyl carbamate in the derivative where R′ = ethyl has known toxicity (EPA 2000).

Bennett 2015; Dobby and Kosick 2013), the froth zone is the last separation stage through which all material that ends up in the launder must flow. In other words, froth zone characteristics directly impact metallurgical outcome. Empirical evidence from plant practice shows that many operational variables can influence froth characteristics to a varying degree. It would be naïve to think that the "froth" is controlled only by the "frother." Even statements such as "collector performance is strongly influenced by froth phase characteristics" begin to lose impact. The influence of chemical and physical-operational factors on froth characteristics (hence, flotation outcome) is easy to observe and demonstrate in the laboratory and plant and is, therefore, testable and self-evident. A change in any reagent or operating condition can change the appearance and properties of the froth zone. Indeed, operators run a circuit by managing the froth zone properties in the plant, though mostly qualitatively through visual observation and experience. For example, a fluctuation in pH, say, by 1 unit (from 10.5 to 9.5) in a copper circuit can have dramatic changes in the appearance and properties of the froth, hence, flotation outcome. Such changes can cover a wide range, from a highly destabilized froth (e.g., no froth layer, and bubbles bursting continually with fizzle) to a very stable froth (either with no mobility or a runaway froth), depending on the ore type and other plant conditions. It is almost impossible to predict this a priori or to generalize this across the industry given our current, limited understanding of the complexity of the froth zone. An extreme example of this complexity might be that a mere change in the addition point of a collector or modifier could have a large influence on froth characteristics, and similarly for other conditions in the plant.

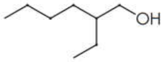
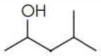
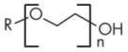
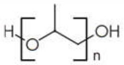
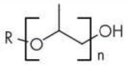
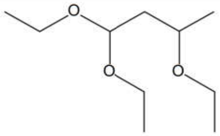
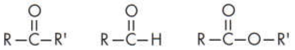
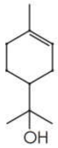
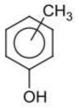
Available frother types. Effective frothers available today fall into one of two categories of compounds: short chain aliphatic (mono) alcohols and polyglycols (see Table 3). The latter includes both unsubstituted and alkyl monoethers (Booth and Freyberger 1962; Klimpel and Hansen 1987; Tveter 1952). Of the thousands of other compounds developed as frothers, certain aldehydes, ketones, ethers, and esters do function as frothers; however, they are not used as primary frothers and are present most commonly as minor components in some frother feedstocks. MIBC is a more widely known alcohol frother and often serves as a benchmark, though it is considered a rather "weak" frother (its strong odor and flammability have also been raised as issues in a few plants). Polyglycols and their ethers, which are considered "strong" frothers, are also widely used. However, the industry is increasingly adopting tailored formulations of alcohol-glycol-glycol ether frothers to meet specific challenges (e.g., frothers for operations with a much coarser primary grind size, or for much finer grind size on finely disseminated ores, or frothers for processing poorer grade/quality ores). Such formulations are most often considered the best compromise to achieve optimum metallurgical outcome; many plants tend to evaluate such combinations on a frequent basis depending on their specific needs. Other notable frothers include cresylic acids (very limited use because of environmental concerns) and alkoxy-substituted paraffins, such as triethoxybutane (TEB; limited use). Pine oil used to be a popular frother until about three decades ago. Its usage has declined substantially. It is used to a limited extent in several plants, notably in China. Hydrocarbon oils are often used in conjunction with alcohols and cresylic acids to modify and stabilize the structure of the froth.

Table 3 lists the most important frothers currently used in flotation operations and their properties. Except for MIBC and 2-ethyl hexanol, commercial frothers are invariably mixtures either by design or by default (i.e., a result of the manufacturing process). Operators generally prefer to control frother independent of other reagents. However, frothers are also often used as a component in collector formulations to produce easy-to-handle products and to aid in physical compatibility of oily and aqueous components. One downside is potential loss in the operator's ability to control froth independently and possibly imposing an upper limit to usable dosage of the collector formulation, since an increase in collector dosage may inadvertently exceed the frother requirement threshold.

Alcohol frothers have very low solubility, whereas most of the glycols (and their ethers) used are completely miscible with water. At the low concentrations used in flotation, solubility and dispersibility are not a limiting factor. Frothing characteristics of alcohol frothers are significantly different from those of glycols, and these differences can be attributed to differences in solubilities, surface activity, critical coalescence concentration (CCC), and diffusion rates.

Guiding rules for frother selection. Currently, selection of frothers and controlling the froth zone in the plants are still based on general qualitative guidelines, empirical testing in the lab or plant to assess performance, visual observations in the plant (often aided by froth visualization cameras), and experience of the operators. An adequate level of practical knowledge of frother selection resides largely with flotation reagent manufacturers and a limited number of industry experts. Frother manufacturer brochures and product lists are a starting point for frother choice; however, invariably one has to rely on an in-house expert from one of the manufacturers, formulators, or consulting companies, and empirical testing, preferably in the plant. Booth and Freyberger (1962) provided an overview of frothers and frothing and summarized general guidelines, but this document is obviously quite old and reflects the lack of attention to the froth zone and frothers in the first 50 years of flotation. In the past three decades, however, there has been a gradual, but healthy, increase in research efforts to understand and model the physics and engineering aspects of froth zone and developing selection criteria for frothers based on quantifiable attributes. Several research groups around the world have contributed significantly and laid the foundation for continued research. A few notable examples of such groups (in alphabetical order) are Aalto University (Finland), Julius Kruttschnitt Mineral Research Centre (Australia), Ian Wark Research Institute (Australia), Imperial College group (United Kingdom), McGill University (Canada), University of British Columbia (Canada), University of Cape Town (South Africa), University of Newcastle (Australia), University of New South Wales (Australia), and University of Queensland (Australia). More recent information on frothers and froth zone may be found in works by Rao 2004; Khoshdast and Sam 2011; Ata 2012; Riggs 1986; Finch et al. 2008; Melo and Laskowski 2006, 2007; Laskowski et al. 2013; Cho and Laskowski 2002; Makhotla et al. 2015; Zhang et al. 2012; Zhou et al. 2016; Cappuccitti and Finch 2008; Zanin and Grano 2006. The vast majority of the studies have been in two-phase systems (i.e., water and air, in the absence of solids), though attempts to

Table 3 Important frothers used in mineral flotation applications

		Properties (values refer to the example structure only)				
Chemical Class	**Structure**	**Example (structure)**	**Molecular Weight, g/mol**	**Density at 20°C, g/mL**	**Water Solubility, g/L**	**Critical Coalescence Concentration, mmol/L**
Aliphatic alcohols	Linear; n = 4–7  $H_3C-[CH_2]_n-OH$	$(CH_3)_2CHCH_2CH_2OH$	88.17	0.815	25	0.29
	Branched: 2-ethyl hexanol 	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	130.2	0.833	4.5	0.122 (based on d50)
	MIBC (methyl isobutyl carbinol) 	$CH_3CH(OH)CH_2CH(CH_3)_2$	102.2	0.807	17	0.11
Poly(ethylene) glycols (PEG), Poly(propylene) glycols (PPG), PPG monoalkyl ethers (MW range: 200–500)	PEG, R=H 	$C_4H_9(OC_2H_4)_3OH$	206.28	0.989	Miscible	0.11
	PPG 	$H(OC_3H_6)_{6.5}OH$	395.6	1.009	Miscible	0.012
	PPGe (R = C_1–C_4) 	$CH_3(OC_3H_6)_3OH$	206.3	0.97	Miscible	0.089
Alkoxy compounds	Triethoxybutane 					~0.11
Ketones, aldehydes, esters (not primary frothers; mostly minor components in feedstocks)	 $R-\overset{O}{\overset{\parallel}{C}}-R'$ $R-\overset{O}{\overset{\parallel}{C}}-H$ $R-\overset{O}{\overset{\parallel}{C}}-O-R'$					
Pine oil (α-terpineol) (limited use)						0.052
Cresols (isomers) (not used anymore)						

Adapted from Nagaraj and Ravishankar 2007

Table 4 Typical qualitative attributes observed for alcohol and glycol* frothers in sulfide flotation*

Attribute	Alcohols	Polyglycols and Glycol Ethers†
Frothing power	Normal alcohols > other isomers; aliphatic alcohols > aromatic alcohols; saturated > unsaturated (opposite in terpene-based)	Strongest frothers; maintain frothing power without staged addition
Bubble size	Larger bubble size, less compact structure	Smaller bubble size, compact structure
Flotation kinetics	Faster kinetics	Slower kinetics
Sensitivity to other conditions	More sensitive to pH; tolerant to slimes	Less sensitive to pH; less tolerant to slimes
Stability	Brittle froth; less tenacity, less persistence; requires staged addition; may cause effervescence at high dosages	Persistent at low dosages; does not require staged addition; breaks down readily in launders; less prone to cause effervescence at high dosages
Selectivity	Lower water retention (greater froth drainage) resulting in greater selectivity; less downstream effects because of selectivity and low persistence	More water retention, lower selectivity, greater downstream effect because of persistence
Coarse particle recovery and load capacity	Less	More

Adapted from Nagaraj and Ravishankar 2007

*The froths resulting from fatty acids, sulfonates, and amine collectors in non-sulfide flotation are often closely textured, stable-bubble aggregates that may not break, even by the application of water jets and sprays. Flotation operators seek to avoid voluminous over-frothing and permanent, lathery froth structures, since these are not conducive to the production of high-grade concentrate and are difficult to handle. The addition of specific frothers along with the non-sulfide collectors are suggested to improve these froth conditions, particularly if large quantities of slimes are present in the ore pulp (Booth and Freyberger 1962; Klimpel 1994; Nagaraj and Ravishankar 2007); however, this may not be generalized and is best evaluated in the plant.

†Triethoxybutane (TEB) produces froths resembling those of pine oil (small-bubble, closely knit texture, lower drainage, lower grades, higher recoveries; breaks down readily in launders). However, like polyglycols, TEB does not flatten froth and produce effervescent froths at high dosages.

characterize the behavior of practical three-phase froths date back to 1930 (Taggart 1947). Results from two-phase studies do not translate well to practical flotation froths, which are dynamic three-phase systems. Several frother attributes have been developed or considered in two-phase systems (e.g., CCC and foam height); however, none of them has been linked to metallurgical outcomes from practical froths (see, for example, Melo and Laskowski 2007; Laskowski et al. 2013).

A system much closer to a plant froth zone is a simulated three-phase system (solid/liquid/gas) in the laboratory. In such systems, it has been clearly demonstrated that a small change in collector, either to a different class or to a different homologue in the same class, can have dramatic synergistic or antagonistic effects on froth characteristics. Such alterations can change an effervescent, loose, watery froth to become a tight, heavily mineralized froth that looks like (flocculated) curds. In extreme cases, heavily mineralized froths can become very dry and sluggish. Adding more or the "right" collector (or frother) may transport more particles to the froth zone, but conversely, adding too much or too strong a collector (or frother) might flatten a froth or destabilize it. Depressing some gangue minerals that were involved in stabilizing the froth might in fact destabilize it. Such effects can be linked to the wettability of solids in the froth zone; however, literature is scarce on this subject.

Importantly, much of the discussion in the literature is related to sulfide flotation where a distinct, designated frother is used, unlike the situation in non-sulfide flotation wherein a designated frother (such as alcohol or glycol) is not always used. In non-sulfide operations, collectors such as long-chain fatty acids and amines generate sufficient froth; however, a judicious use of a frother can often lead to significant metallurgical improvement. Although the overall froth zone properties are determined by collectors, modifiers, and other chemical and physical factors, a separate for-purpose chemical is still necessary in virtually all sulfide flotation systems to provide the basic froth. It is widely believed, though somewhat inaccurately, that most of the sulfide collectors, both water-soluble and water-insoluble, are (essentially) nonfrothing because of their shorter chain lengths and, therefore, require the use of specific (or designated) frothers. Some sulfide collectors, under certain specific conditions, are capable of producing froth that is sufficient to operate a circuit for a period of time—for example, the dithiophosphates, especially the longer-chain, water-soluble dialkyl and dicresyl dithiophosphate salts, and the oily dicresyl dithiophosphoric acid. Sometimes, the residual alcohol in these collectors contributes to froth formation as well. However, plants cannot rely on a collector alone to operate a circuit. More importantly, however, the use of frothers in these systems is predicated on the necessity to float coarse (100–250 µm), heavy particles (specific gravity 3.5–19)—both liberated and middlings—and to produce a froth zone that can support such particles (Klimpel and Hansen 1987). A judicious choice of frothers is also predicated on the need to target a certain mass pull (or selectivity).

Qualitative attributes of various alcohols and glycols are shown in Table 4. Impurities in frothers, even in small quantities, sometimes have a marked effect on frothing power and froth structure. Highly insoluble components are frequently observed to float off with the froth, to concentrate in localized areas at the froth surface, and to depress frothing (Booth and Freyberger 1962).

Parameters that affect and are used to describe froth zone characteristics are listed in Table 5. Operational variables, froth characteristics, and qualitative descriptors are listed in Table 6.

Operators manipulate chemical addition and process parameters to achieve multiple concomitant goals in an optimally performing flotation circuit. General goals are listed here, although the importance of each goal may vary from operation to operation:

Table 5 Froth zone parameter definitions

Parameter	Definition	Defining Equation	Units	Typical Range
Q_A	Volumetric air flow rate		L/min	
d_s	Bubble size (surface diameter)		μm	
d_v	Bubble size (volume diameter)		μm	
d_b	Bubble size (diameter); Sauter mean bubble diameter, d_{32}		μm	1,000–3,000
n	Number of bubbles per unit time		1/s	
S	Bubble surface area	$\pi \cdot d_b^2$	m^2	
J_g	Superficial gas rate or velocity [A = cross-sectional area of cell]	Q_A/A	m/s	0.001–0.03
S_b	Bubble surface area rate or flux	$[n \cdot S/A]$ or $[(Q_A)/(\pi/6 \cdot d_b^3)]$ or $[6J_g/d_b]$	1/s	30–100
C_a	Froth carrying capacity (rate of concentrate floated per unit cross-sectional area): d_p = particle diameter (m) ρ_p = particle density (kg/m^3)	$\pi \cdot d_p \cdot \rho_p \cdot J_g/d_b$	$t/h/m^2$	1–5
k	Overall flotation rate constant: R = recovery at time t R_∞ = ultimate recovery ($t = \infty$)	$-\ln[1-(R/R_\infty)]/t$	1/s	
K_c	Collection zone flotation rate constant (zero froth depth)	$-\ln[1-(R/R_\infty)]/t$	1/s	
R_f	Froth recovery	k/K_c	—	
h	Froth depth		m	0.05–0.5 (mechanical cells); 5–10 (column cells)
τ_f	Froth retention time index	h/J_g or $h \cdot A/Q_A$	s	
ε_g	Gas holdup (or froth factor); volume of bubbles/total pulp volume		%	10%–20% in mechanical cells
ε_w	Water holdup (volume fraction of water in the froth)		%	
ε_s	Solids holdup (volume fraction of solids in the froth)		%	
R_f	Froth recovery factor (efficiency with which particles arriving at the froth–pulp interface reach the concentrate). P is the mineral floatability factor.	$k/(P^* S_b)$	%	

Table 6 Operational variables, froth characteristics, and qualitative descriptors

Operational Variables	Measurable Froth Characteristics	Qualitative Descriptors*
• Type, amount, and addition point of frother(s) • Type, amount, and addition point of collector(s) • Type, amount, and addition point of modifier(s) • Ore type and mineralogy • Particle size distribution • pH • Presence of slimes • Airflow rate • Hydrodynamics in the cell • Pulp level density • Water chemistry (dissolved inorganic salts, organic matter)	• Bubble size • Volume (height or depth) • Texture • Mobility • Stability • Persistence • Rheology • Carrying capacity	• Well-knit, close-knit • Watery, wet or dry • Lots of windows, clean windows • Stable • Evanescent (quickly fading) • Effervescent (unstable froth, creating a mist over froth surface) • Persistent • Sticky • Brittle • Free-flowing, mobile • Selective, nonselective • Loose • Lathery

Adapted from Nagaraj and Ravishankar 2007
*Common terms used by plant operators.

- Mass pull, mass flow, and grade targets
- Manageable and consistent froth characteristics down the entire bank of cells
  - Steady, uniform, and appropriate volumetric flow of froth from cell to launder.
  - Full mineralization, or, if partial mineralization, the windows on bubbles are clear (i.e., water film is not dirty with fine gangue).
  - Rougher cells exhibit good mass pull and high grade in the first few cells.
  - Cells at the end of the rougher bank are barren, yet there is still some manageable amount of froth.
  - No flooding occurs in the first or second cleaner; no or low insols in the cleaner circuit. (Insols are materials that are insoluble in acid digestion. They are a proxy [i.e., an incomplete accounting] for non-sulfide gangue and typically underestimate the total concentration of gangue in a sample.)
  - No froth occurs in the concentrate and tailings thickeners.

Operators typically employ combinations of frothers to manage and control their circuits. Those combinations and doses can vary across the flotation circuit. In addition to choice of frother, operators can alter the addition points of the frother. For example, frother is rarely added to the grind and more commonly to the head of the rougher circuit. Some frother may also be added to the scavenger circuit if the froth there is inadequate or if the tails assay (for value minerals) is too high. Frothers may even be used in the cleaner circuit; however, such use depends on the frother carried over from the rougher-scavenger circuit and frother coming from circulating loads.

The attribute of froth texture is a little more difficult to put in quantitative terms; however, operators have their own descriptions of froth texture, which become part of their experiential knowledge. These descriptions are nonetheless quite valuable in guiding the changes they make to the flotation system. Booth and Freyberger (1962) noted that froth structure or texture has a strong influence on recovery and grade: "Small-bubbled, closely knit froths will be conducive to high recovery; such froths support heavy mineral loads and prevent detachment of values from the froth. On the other hand, a loosely textured, larger-bubbled froth will tend to release gangue particles from the bubble aggregate and tend to produce concentrates of higher grade."

Another parameter that features importantly in managing and controlling a flotation circuit is pH. Many statements and generalizations about the effects of pH on froth appearance and behavior are prevalent in the industry. However, they are rarely linked to fundamental concepts and should be viewed with caution since they only provide information for specific systems and conditions and lack universality.

Klimpel and Hansen (1987) noted:

> It is sometimes assumed (especially in laboratory studies) that the choice of frother type and dosage is not as crucial as some of the other factors such as collector type and dosage. Plant practice does not support this assumption. Significant improvements can be achieved by managing froth phase, i.e., frother type and dosage. The scientific fundamentals involved in froth development and stability in the presence of particles and turbulence are extremely complex and not yet fully developed; consequently, a priori predictions of performance cannot be made for a given frother. Sometimes, a higher frother dosage, rather than higher collector dosage, is used to improve value recovery because frothers generally have lower unit price, in spite of the fact that this invariably produces poor selectivity.

Rao (2004) observed the following: "It is obvious that despite a considerable amount of attention being paid in the last 100 years to the characteristics of bubbles, of thin layers separating these bubbles in foams and froths, and of the lifetime of froths, there is no unanimity regarding parameters that govern the stability and the collapse of froths." Therefore, research is critically needed in the three-phase froths with direct relevance to plant systems.

Ultimately, frother performance is judged based on the metallurgical outcomes: value mineral recovery, by-product or co-value recovery, concentrate grade, rejection of penalty elements, reduction in mass pulls, ease of operation (in terms of managing froth stability, mobility), carrying capacity, rejection of gangue minerals (particularly those resulting from entrainment and entrapment), cost, and possibly some others specific to an operation.

Reagents for Non-Sulfide Minerals

With the exception of a few elements such as the base and precious metals, which are predominantly obtained from sulfides ores, most other elements or their minerals are obtained from non-sulfide ores. A chronology of reagent development of relevance to plant practice in non-sulfide flotation may be found in Nagaraj and Ravishankar (2007; Table 1 therein), and Nagaraj and Farinato (2014, 2016).

Aplan (1994) noted that the non-sulfide flotation literature is very fragmented. This is necessarily so if one considers the variety of non-sulfides that are beneficiated in the industry and the artisanry that surrounds these processes. However, as in sulfide flotation, a common theme emerges if one considers the types of reagents used (both collectors and modifiers) and the types of treatment methods employed. Redeker and Bentzen (1986) noted that "Flotation of nonmetallic minerals is sometimes viewed as alchemy. However, the art is, in reality, based on sound chemistry, experience and a little luck in the treatment of new ores. In the flotation of nonmetallic ores, as opposed to base metal sulfides, highly specific treatment conditions are required to accomplish separations." Aplan and Fuerstenau (1962) noted that "Selective flotation in non-sulfide systems is often difficult in that one class of compounds alone, the carboxylic acids, may float nearly the entire array of non-sulfide minerals under the appropriate conditions. The non-sulfide mineral flotation operator is confronted with a vast array of modifying reagents."

In the case of sulfide flotation, a wide variety of collectors, many of which exhibit a high degree of selectivity for a given sulfide, is available for the relatively small number of sulfide minerals floated. In contrast, only a small number of collectors, many of which are rather nonselective, are available for the large number of non-sulfide minerals floated. Indeed, modifiers sometimes assume a greater role than collectors in non-sulfide separations, and it is common to use several modifiers in a given separation. This obviously complicates the system considerably, puts it in the realm of art form, and makes it very challenging for a scientific study.

Pulp preparation prior to flotation separation is far more important in non-sulfide separations. This includes one or more of the processes such as washing and/or attrition scrubbing (usually with acid or alkali), blunging (typically for clays), desliming, hot pulp conditioning, and high solids conditioning. Preconditioning requirements are often less stringent in flotation with amines, in contrast to flotation with fatty acids. Conditioning in amine flotation is usually at the same pulp densities (~20–30 wt %) as flotation, unlike in fatty acid or sulfonate flotation wherein pulp densities could be as high as 70–75 wt %. A variety of modifiers is used in these operations to ensure that collectors added subsequently adsorb selectively onto the desired minerals. The critical factors are pH, contact time of reagents, agitation intensity, water quality, and frequently the temperature during scrubbing, conditioning time, and the number of conditioning and flotation stages.

Conditioning times with amines and petroleum sulfonates tend to be short (e.g., 30 seconds to 2 minutes), whereas for fatty acids and alkyl hydroxamates, conditioning times vary considerably, from 30 seconds to 30 minutes, depending on the particular separation.

Desliming is a very common and often critical step in non-sulfide flotation circuits, unlike in sulfide mineral flotation, because the slimes, being non-sulfide minerals (clays, iron oxides, etc.), can increase collector consumption, coat coarse particles, hinder particle attachment to bubbles, and seriously interfere with separations. The presence of slimes can reduce the ability of collectors to selectively adsorb onto targeted mineral surfaces. Since these slimes are usually discarded, they can account for a considerable loss in value minerals. The deslimed material is sometimes separated into coarse and fine fractions and treated separately to optimize flotation conditions for each size fraction. Some non-sulfide separations are virtually impossible if the feed to flotation is not properly deslimed. The term *slimes* has a loose meaning in non-sulfide separation and is system dependent. For example, –100 µm particles are considered as slimes in some phosphate operations, whereas in other systems, particles less than 1–10 mm are considered slimes.

Compared to sulfide flotation, the field of non-sulfide flotation is almost bewildering in terms of the diversity of separations and technologies employed. However, general guidelines are available in published literature and chemical supplier handbooks (Redeker and Bentzen 1986; Cytec Industries 2010; Arbiter and Williams 1980; Yang 1987; Holme 1986; Davis 1985). These are excellent starting points, and the practitioner must then conduct empirical testing to make the necessary changes to reagent schemes and processing schemes dictated largely by the mineralogy, particularly that of gangue minerals. The general approach to laboratory testing is provided in a separate chapter of this handbook.

Collectors

In stark contrast to sulfide flotation, two types of collectors, namely fatty acids and amines, cover approximately 90% of the separations in non-sulfide systems. The usage of collectors, excluding auxiliary collectors such as hydrocarbon oils, in non-sulfide flotation follows the order: fatty acids > amines > petroleum sulfonates > other surfactants. In recent years, there has been growing interest in the development of specialty collectors that have the potential to provide significantly improved performance. A great example is that of alkyl hydroxamates (discussed later in this chapter). The important active donor atom in almost all of the collectors is still the O. The important classes (or families) of collectors used in non-sulfide mineral flotation are listed in Table 7. Only generic v structures and typical chain lengths are given because, in practice, most of the reagents tend to be mixtures either resulting from the manufacturing process or deliberately formulated by chemical suppliers; exact compositions may not be available for these, whether for lack of analysis or proprietary reasons.

Fatty acids. Fatty acids can be considered to be almost universal collectors, because they can be made to float almost all minerals; consequently they tend to be nonselective. The use of appropriate modifiers alleviates this problem somewhat and allows even difficult mineral separations. Fatty acids can also be used to float sulfides, but they offer no advantages over the S-containing compounds that are much more selective for sulfides than are fatty acids. Fatty acids, however, have been used for the recovery of oxide copper minerals, though this is not widespread because of the poor selectivity and often the presence of several multivalent ions in the plant water (especially alkaline-earth ions, which can precipitate as fatty acid soaps).

Two main sources of fatty acids are oils and fats from vegetable and animal sources (tallow), and wood pulp (tall oil fatty acids or TOFA). Composition of fatty acids varies depending on the source. Fatty acids are best characterized by their iodine value (IV) and acid number (AN). IV indicates the amount of unsaturation in the molecule (i.e., the number of double bonds). AN is a measure of the amount of carboxylic acid groups in the product. TOFA and crude tall oil (less expensive than TOFA) are the most widely used. The composition of crude tall oil varies greatly, depending on the wood used (acid numbers can vary in the range of 125 to 165, depending on the wood used). By fractional distillation of crude tall oil (with rosin content of ~40% or higher), higher-grade fatty acids (with reduced rosin content) is obtained. A good quality TOFA is a distillation product with rosin content 10% or less. TOFA consists mostly of oleic acid. The choice between TOFA and crude tall oil is dependent on the price tolerance of a particular operation, though the performance of crude tall oil is typically less than that of TOFA. Suppliers may also market formulations of fatty acids with various additives; composition of such formulations is most often proprietary.

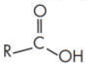
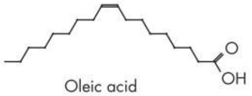
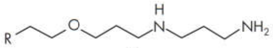
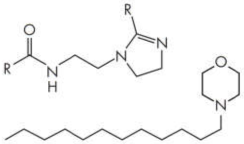
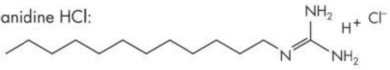
Amines. Five types of amine collectors can be recognized (see Table 7): (1) fatty acid condensate amine (and imidazoline), (2) alkyl ether amine (and diamine), (3) alkyl morpholine, (4) fatty amine, and (5) alkyl guanidine.

Typical dosages for amines are 0.05 to 0.5 kg/t. They generally require short conditioning time as they are known to have rapid adsorption. Amines are effective in a wide pH range (2.5–10.5), and the choice of the pH depends on the mineralogy and the required selectivity—for example, direct flotation of sylvite (KCl) in sylvite–halite (NaCl) separation; reverse flotation of halite in carnallite–halite separation; feldspar and mica flotation at pH 2.5–3.5; silica flotation from phosphate at pH ~ 6.5–7 (phosphate mineral depressed using sulfuric acid, starch, and others), and silica flotation from hematite at pH ~10.5 (hematite depressed using starch; silica activated and slimes dispersed using sodium silicate). Amines are often used in reverse flotation processes, that is, when the gangue (e.g., silica) is floated away from the value minerals.

Amines are characterized by amine number, which is a measure of the amount of amine groups and used to estimate the average MW. This is especially useful when the collector product is a mixture of amines and often with other formulation components. It is determined by titration of the amine acetate with hydrochloric acid (HCl).

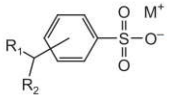
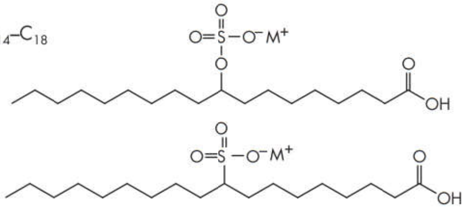
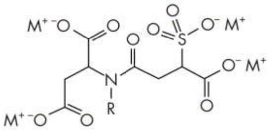
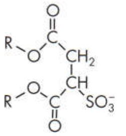
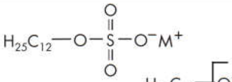
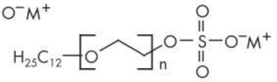
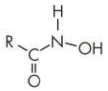
Natural and synthetic petroleum sulfonates. The family of sulfonates and sulfates (all anionic surfactants; Table 7) is quite large. Several products from this family have been used extensively in flotation applications, and these constitute the third largest group (after fatty acids and amines) of collectors used in non-sulfide flotation. Natural petroleum sulfonates are manufactured by sulfonation of crude oil, crude distillates, or any portion of these distillates (Basu and Shravan 2008). Synthetic sulfonates are made by alkylation of an aromatic hydrocarbon with a selected olefin, followed by sulfonation

Table 7 Collectors used in non-sulfide mineral flotation*

No.	Chemical Class	Structure	Plant Application
1	Fatty acids	R = C_{14}–C_{18}   Oleic acid	Widely used for beneficiation of phosphates, fluorspar, kaolin clays; glass sands, heavy mineral sands, foundry/molding sands, kyanite, tungsten ores, and to a limited extent low-grade iron ores; common example is tall oil containing palmitic acid (C16:0), oleic acid (C18:1 cis-9), linoleic acid (C18:2 cis,cis-9,12). C_{18} unsaturated fatty acids (e.g., oleic, linoleic, and linolenic acids) are the most efficient collectors in tall oil mixtures. Long-chain saturated fatty acids (>C_{12}) are poor collectors (attributed to their much lower solubility and increasingly high melting points; Hsieh 1980) and, therefore, are not used as primary collectors (there may be small amounts of saturated fatty acids in commercial fatty acid products). Dosages vary from 250–3,000 g/t depending on the ore system and target mineral. Conditioning times vary from 30 seconds to 30 minutes. High solids (50–75 wt %) conditioning is typical, sometimes at high temperature (e.g., fluorite and kaolin).
2	Amines and their salts	Fatty amines:  Amine salt: $R{-}NH_3^+\,Cl^-$ Condensate amines:  Alkyl ether amine:  Alkyl ether diamine:  Alkyl imidazoline: Alkyl morpholine:  Dodecyl guanidine HCl: 	Typical R = C_{12}–C_{18}; widely used for the beneficiation of potash, iron ore, phosphate, calcium carbonate, feldspar and other silicates, and silica sand. Primary fatty amines, ether amines, and condensate amines constitute the bulk of cationic collector usage in the industry. Alkyl morpholine is used in the halite flotation from carnallite salts. Ether amines and ether diamines are used predominantly to float silica in Fe ore beneficiation. Ether amines are typically $C_{12–14}$ and are considered to have slightly weaker collecting property and therefore higher selectivity. Amines are typically pastes, difficult to handle, and have poor solubility and dispersibility. Consequently, they are used as custom blends of amine or its salt (e.g., full or half acetate) and frothers or other diluents (e.g., hydrocarbon oil, surfactants); these are used as dilute dispersions (1%–5%). Plants may prepare the salt on-site. Formulations provide more flexibility. Their composition is often proprietary. Ether amines are liquid products, more soluble and dispersible. Diamines tend to be stronger because they contain two N atoms (one secondary and the other primary), but they are also known to be more frothing.

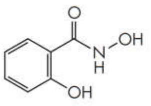
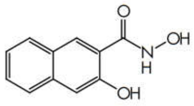
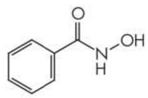
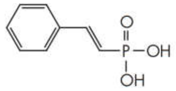
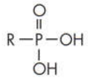
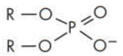
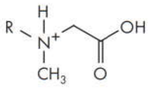
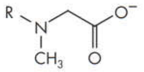
(continues)

Table 7 Collectors used in non-sulfide mineral flotation (continued)

No.	Chemical Class	Structure	Plant Application
3	Petroleum sulfonates MW ~300–550		Widely used for removal of iron and other contaminants in the processing of glass sands, feldspar, and other ceramic raw materials. Also in formulations with fatty acids. Combinations of low- and high-molecular-weight compounds, or of synthetic and natural sulfonates, are also used commonly. Products tend to be viscous liquids or pastes that require specific reagent preparation steps such as tanks equipped with heaters and intense agitation to solubilize or disperse. Typically supplied as custom formulations that provide better handling characteristics and better metallurgical performance at reduced dosages.
4	Sulfated and sulfonated fatty acids	R = C_{14}–C_{18} 	Used for reverse flotation of carbonates from phosphate ores in the pH range of 5–5.5 (Lawendy and McClellan 1993). These collectors are known to be more tolerant to Ca and Mg ions and, therefore, particularly useful in waters with high hardness.
5	Alkyl sulfosuccinamates	R = C_{12}–C_{18} 	Mostly used for specialty applications, often in combination with fatty acids and petroleum sulfonates. They are used in the beneficiation of barite, fluorspar, scheelite, phosphates, cassiterite, wollastonite, celestite, and glass sands.
6	Dialkyl sulfosuccinates	R = C_6–C_8 	Mostly used for specialty applications, and in combination with fatty acids.
7	Alkyl sulfates Alkyl ether sulfates	 	Limited use; frequently in combination with fatty acids (e.g., barite ore beneficiation).
8	Alkyl hydroxamic acids	R = C_8–C_{10} 	Mostly for specialty applications; sometimes combined with fatty acids. Important applications include kaolin clay (especially fine clay) beneficiation (colored mineral removal without activators or carrier minerals), rare earths, oxide copper minerals from oxide/sulfide/mixed ores.

(continues)

Table 7 Collectors used in non-sulfide mineral flotation (continued)

No.	Chemical Class	Structure	Plant Application
9	Aryl hydroxamic acids (e.g., salicyl-, hydroxynaphthyl-, and benzo-hydroxamic acid)	  	Limited use currently; rare earths and oxide Cu beneficiation.
10	Aryl and alkyl phosphonic acids	Styrene phosphonic acid (SPA)  R = C_8  $\mathrm{R-P(=O)(OH)-OH}$	SPA used widely in cassiterite flotation; high unit cost of SPA is often offset by unique selectivity and efficiency. No other use.
11	Dialkyl phosphates	R = C_8 	Very limited use (e.g., selective separation of phosphates from siliceous and carbonate gangue).
12	Amphoteric collectors	(low pH) R typically C_{12} (high pH)  	Very limited use (e.g., selective separations between phosphate, silica, and carbonate gangue); removal of phosphate impurities from iron ore.
13	Hydrocarbon oils (kerosene, diesel oil, burner oil, gas oil, fuel oil, pump oil, vapor oil, aromatic oils, vegetable oils, mineral oils)	Complex mixtures of aliphatic hydrocarbon, aromatic hydrocarbons, linear and branched. Carbon number range: C_8–C_{22}	Flotation of naturally hydrophobic minerals (talc, sulfur, graphite and other forms of carbon). Extender to fatty acids, amines and other collectors. Froth modification and control.

*Only generic idealized structures and typical chain lengths are given.

of this alkylate (Malmberg et al. 1982). In general, natural petroleum sulfonates are much more complex mixtures than synthetics (Basu and Shravan 2008). Petroleum sulfonates were originally developed as relatively inexpensive anionic collectors to selectively concentrate iron-bearing minerals in low-grade iron ores and to remove iron and other mineral contaminants by flotation in the processing of glass sands, feldspar, and other ceramic raw materials. Further development resulted in additional reagents with a broadened application to the selective flotation of a variety of non-sulfide minerals (Holme 1986; Falconer 1961).

Sulfated and sulfonated fatty acids. These date back to the mid-1800s, developed primarily as textile additives and soap. They are produced by reacting fats, oils, and tall oil with sulfuric acid or oleum or SO_3, sulfuric trioxide (current practice), followed by hydrolysis and saponification using sodium hydroxide. This results in addition of a sulfate or sulfonate group at the double bond in unsaturated fatty acids. The terms *sulfated* and *sulfonated* are used interchangeably, though they are chemically very different—sulfated species having the sulfur attached to the hydrocarbon chain via an oxygen atom (Table 7). The formation of a sulfate or sulfonate is determined largely by whether sulfuric acid or oleum or SO_3 is used and by the process conditions. Further complexity arises from the extent of hydrolysis and saponification. Sulfonated (sulfated) fatty acids are typically complex mixtures, and their characterization is often not readily available.

Sulfosuccinates and sulfosuccinamates. Sulfosuccinamates (Table 7) were introduced originally in 1945 for non-sulfide flotation and more formally in ~1965 as collectors for cassiterite flotation (Arbiter and Hinn 1968), and subsequently for the flotation of a wide variety of non-sulfide minerals, either alone or in combination with fatty acids and petroleum sulfonates (Day and Hartjens 1974, 1977). Industrial practice indicates that they have unique properties and provide synergistic effects with fatty acids and petroleum sulfonates. For example, when used in combination with fatty acids, at a level of ~10%–20% of the fatty acid dosage, they provide better froth structure and higher recovery of fine and coarse particles in phosphate flotation. They also serve to emulsify the fatty acid, thereby improving its performance and providing a stabilizing effect on the plant performance differences resulting from pH, fatty acid grade, and feed grade variations.

Alkyl hydroxamates. Alkyl hydroxamates (Table 7) were first suggested for flotation in 1941 (Pöpperle 1941), and their utility was expanded in the 1950s through 1970s, but plant usage was sporadic and minor, mostly in the old Soviet bloc. There is currently extensive literature on both fundamental studies and potential applications of alkyl hydroxamates for flotation of a wide variety of minerals (Fuerstenau and Pradip 1984; Assis et al. 1996; Hughes et al. 2007; Bhambhani et al. 2016; Jordens et al. 2016). Their usage prior to 1980s was rather limited. Two important innovations in the 1980s appear to have changed this situation. First was the use of alkyl hydroxamate for removing colored impurities from kaolin clays (Yoon and Hilderbrand 1986a, 1986b). The second was the development of a practical, safe, and economical process for the manufacture of alkyl hydroxamates (Wang and Nagaraj 1989), which resulted in a clean liquid product that was stable and easy to handle. Additional developments occurred in the manufacture of alkyl hydroxamates (Hughes 2004, 2006; Bhambhani et al. 2017). In addition to C_8–C_{10} alkyl hydroxamates, three other hydroxamic acids are now available: salicyl-, hydroxynaphthyl-, and benzo-hydroxamic acid (Wu and Zhu 2006; Jordens et al. 2016; Xia et al. 2015). However, their plant usage appears to be limited.

Although hydroxamates and hydroxamic acids are structurally closest to fatty acids (hydroxamates have the additional –NH in the functional group), their solution chemistry and interactions with minerals are vastly different from those of fatty acids (Nagaraj 1987; Fuerstenau et al. 1970). One of the most important differences is that hydroxamates are far more selective than fatty acids under most conditions.

Phosphonic acids, phosphoric acids, amphoterics, and hydrocarbon oils. The most well-known phosphonic acid is styrene phosphonic acid, or SPA (Table 7), which has shown some unique properties (Andrews 1989, 1990; Wottgen 1969). This is used in cassiterite flotation. One cheaper alternative, an amino phosphonic acid, has been successfully used in a tin operation (Codd 1984). There does not appear to be any other commercial use for SPA. Other phosphonic acids have been proposed (Wottgen and Lippman 1963), but none have found significant application.

Alkyl phosphoric acid esters have found niche applications, usually in conjunction with other collectors. Houot (1983) describes their use in selective separation of phosphates from siliceous and carbonate gangue. In one case, for example, the phosphates and carbonates can be floated into a bulk concentrate using alkyl phosphates, leaving the silica in the tails. The bulk concentrate is then scrubbed with sulfuric acid to selectively strip the collector off the phosphate surfaces and the carbonates are floated without any additional collector. In another case, the carbonates can be floated selectively with alkyl phosphates using sodium fluorosilicate or sulfuric acid as a depressant for phosphates. The silica remaining with the phosphates can then be floated selectively using an amine collector.

Amphoteric collectors have some unique properties and provide the potential for achieving selectivity over a wide range of pulp conditions.

Sodium N-n-dodecyl sarcosinate has been used commercially for selective separations between phosphate, silica, and carbonate gangue. Although reportedly used in Siilinjarvi, Finland (Chadwick 1981), there does not appear to be a widespread application of this collector. One of the important reasons could be the higher cost of the product compared to the fatty acids and amines used in phosphate beneficiation. Amphoteric collectors have also been used to remove phosphate impurity from iron ores. One advantage with an amphoteric collector is that the same reagent can be used at two different pH values to float different mineral species.

Large amounts (and high dosages) of hydrocarbon oils such as fuel oil, diesel oil, and kerosene are used in non-sulfide flotation as extenders or auxiliary collectors to enhance the flotation with fatty acids, amines, and petroleum sulfonates. Overall tonnage used is more than that of fatty acids.

Frothers

Because the collectors used in non-sulfide flotation provide adequate froth formation, the use of *separate* frothers (short chain alcohols and polyglycols) is generally not widespread. When used judiciously, frothers have been shown, however,

Table 8 Interaction of modifiers with minerals and the mechanism of modification of floatability

	Adsorption Phenomena
1	Adsorption of ions: electrostatic, specific adsorption, adsorption of potential determining ions (e.g., M^{n+} on oxides and sulfides; OH^- on sulfides or oxides, which then affects collector adsorption; HS^- on sulfides [driven by solubility product, chemical reaction])
2	Ion exchange and chemical reaction; Cu activation of sphalerite
3	Entropy-driven adsorption (due to bound counterion release; e.g., adsorption of polyacrylate on iron oxides)
4	Hydrogen bonding and hydrophobic bonding (e.g., adsorption of nonionic species on minerals, especially nonionic polymers)
5	Chemisorption and chemical reaction (e.g., NaCN [sodium cyanide] on sulfides, polyacrylate on calcite or apatite)
	Mechanism by Which a Modifier Can Affect Mineral Floatability
1	Selective blocking of all active sites to prevent collector adsorption (PO_4^{2-} on apatite preventing fatty acid adsorption)
2	Inadvertent activation and the consequent adsorption of collector (the active centers are not of the mineral but are of the impurity species causing inadvertent activation)
3	Concentration-dependent effect: At low concentrations sodium sulfide can activate certain oxides and tarnished sulfides, and at high concentrations it depresses these.
4	Adsorption of colloidal reaction products of modifiers on minerals (e.g., metal sols of sodium silicate, products of solution hydrolysis, sol formation and gel formation, or other colloidal precipitates)
5	Prevention of heterocoagulation of slimes to minerals (e.g., with dispersants such as polyacrylate, and polyphosphate)
6	Removal of active species (sites) from the surface by complexation. This is often concentration dependent. At low concentrations, certain complexing reagents can chemisorb on surfaces, but as the concentration increases, they can form soluble complexes that are then released into solution. NaCN is a good example; another example is polyphosphate.
7	Removal of hydrophobic species from surfaces. Chemical or physical methods. For example, Na_2S in Cu-Mo separation—removal of collectors from surfaces. Removal of oleate from apatite by sulfuric acid. Layers of mineral may be removed in this process. Physical means would be steaming, high-energy attrition.
8	Removal of hydrophilic patches to increase floatability, (e.g., sodium sulfide, dispersants). For example, a layer of limonite may be removed from the oxidized surface of chalcopyrite by treatment with oxalic acid and subsequent washing with water. Acid scrubbing of many sulfide and non-sulfide minerals and of glass sands to activate iron-bearing impurities and remove such impurities from silica surfaces. Treatment of beryl with hydrofluoric acid (HF) leads to removal of the silicate components such as silica and alumina, thereby increasing Be concentration on the surface.

Adapted from Nagaraj and Ravishankar 2007

to contribute to improved performance (e.g., better froth control, carrying capacity, and recovery of coarse and fine particles) in the beneficiation of phosphate, glass sand, feldspar, soluble salt, and calcium carbonate. Frothers are also often a component in collector formulations (e.g., those of fatty acids or amines) to produce easy-to-handle products and to aid in physical compatibility of oily and aqueous components. In some cases, however, when frother is already a part of the formulation, it reduces the ability to control froth independently and may impose an upper limit to dosage of the collector formulation (because an increase in collector dosage may inadvertently exceed the frother requirement threshold).

Kerosene and fuel oil are often used to effectively control the voluminous over-frothing caused on occasion by saponified fatty acids and tall oils.

Modifiers

This section discusses the broad collection of modifiers that can be used in both sulfide and non-sulfide mineral flotation. Unlike collectors, understanding modifier chemistry and complex interactions presents a formidable challenge; this is exacerbated by the limited coverage and discussion in the literature for modifiers that are of relevance to plant practice. The intent is to give relatively greater coverage to modifiers in this section.

Of the three major reagent categories forming the flotation reagent triangle, modifiers have perhaps the greatest effect on rate of flotation of particles; in the extreme, flotation is completely suppressed. This effect can be either positive or negative, and it can be temporary (i.e., the mineral can be refloated in another stage with relative ease, such as when using a polymeric modifier) or permanent (i.e., true depression, where the mineral can be refloated only after stronger measures have been taken, such as a change in chemical environment; for example cyanide depression of pyrite or sphalerite, reversed by addition of copper sulfate). Thus, one modifier may merely decrease the flotation rate of one mineral selectively and sufficiently so that selective flotation of another mineral is possible.

Modifier Function and Mode of Action

Modifiers are used to create and/or magnify the differences in the surface properties of minerals subject to separation. The overall action of modifiers on flotation is manifested in the activation or depression of individual minerals, allowing an increase in flotation selectivity. Modifiers can often participate in a variety of processes. The dominant forms of modifier action are those that proceed most rapidly and whose physical results have the greatest effect on the state and properties of the solid surfaces and air bubbles, and on pulp chemistry. The action of most modifiers on minerals is strongly influenced by the particular conditions in the reagent conditioning and flotation stages, and by the ore composition. Modifier action is best understood by determining their dominant effects on the individual subprocesses in a flotation system.

The chemistry of modifiers in flotation pulps is quite complex in comparison to that of collectors, and it is more complex in non-sulfide systems than it is in sulfide systems. The interactions of modifiers with minerals and the mechanism by which modifiers affect mineral floatability and selectivity are summarized in Table 8. Modifiers can affect multiple factors simultaneously in flotation pulps and, therefore, can have multiple functions (details of *predominant* functions of various modifiers are found in Eigeles 1977, Laskowski 1988, and Chander 1987). For example, addition of lime in a copper circuit can have the following effects:

- pH modification (and the resultant changes in interfacial chemistry, solubility of minerals, changes in water chemistry)
- Depression of pyrite
- Formation of colloidal calcium sulfate precipitate and its interaction with sulfide minerals

- Modification of froth characteristics and viscosity of pulp, thereby altering particle transport through froth, gas dispersion, and bubble–particle interactions
- Modification of collector adsorption
- Precipitation of multivalent metal ions as hydroxides
- Removal of slime coatings from sulfides
- Dispersion and depression of certain gangue minerals
- Reduction in grinding media wear

Thus, depending on the type, modifiers can change pH, pulp potential (E_p), composition of the aqueous phase, surface composition of the minerals and bubbles, and froth characteristics; in other words, they can affect properties of all three interfaces. Modifiers change mineral surfaces either directly by adsorbing at the solid–liquid interface (via physical or chemical adsorption) or indirectly by changing aqueous phase composition. Modifiers can also affect the liquid–gas interface (thus, froth characteristics) significantly, but this aspect has been inadequately studied. They are also known to affect dispersion and rise-velocity of bubbles. The same modifier (e.g., lime) in different circuits could produce very different flotation outcomes, or different modifiers used for pH control in a circuit can have very different results at the same nominal pH (e.g., lime versus NaOH).

The action of modifiers (alkalis, acids, and salts) on the dispersion of air bubbles and the intensity of frothing was described long ago (Gaudin 1957). The strong effect of pH on froth stability and mobility is all too well known in sulfide circuits, and the direction and magnitude of this effect is strongly influenced by gangue mineralogy and is quite variable. Generalizations are difficult to make. Salts of multivalent metals, such as copper and iron, even at low concentrations, reduce the stability (and/or mobility) of the froth formed by an alcohol; the magnitude of the effect is strongly influenced by pH. Thus, copper sulfate is often used to control excessive froth in certain sulfide circuits. In a zinc circuit, after the addition of copper sulfate and xanthate, a decrease in frothing is sometimes observed, and this can be restored after the addition of lime (Eigeles 1977). Slimes and colloidal precipitates that exist in flotation pulps strongly influence the froth zone and bubble–particle interactions. Their effect can be moderated by modifiers as well. Thus modifiers can affect froth flow, and particle transport from pulp into froth and from froth into launder.

In many cases, modifiers can have multiple modes of action. Some examples are shown in Table 9. The following general categories of modifier mode of action are illustrated with examples.

Classes of Modifiers

Modifiers fall into two groups: unintended and deliberately added chemicals. Deliberately added modifiers can be classified as inorganic, small organic, or polymeric reagents. Inorganic modifiers, which are the least expensive (unit price or price per kilogram) and have been around the longest, are used the most. Many small organic modifiers can provide good performance; however, their higher treatment cost relative to inorganic modifiers often limits their use. Polymeric modifiers include natural product-based (e.g., polysaccharides, tannins, and lignin) and synthetic low-MW polymers that have mineral-specific functional groups incorporated into the polymer (Nagaraj et al. 1987; Nagaraj 2000; Aimone and Booth 1956). Synthetic modifiers can be specifically tailored by incorporation of various functional groups to provide selective separations (Nagaraj 2000). With this ability, synthetic modifiers can help improve the sustainability of challenging separations and potentially serve as attractive alternatives to some hazardous chemicals currently in use. Polymeric modifiers typically require significantly lower doses compared to inorganic and small organic modifiers, making them more cost-effective.

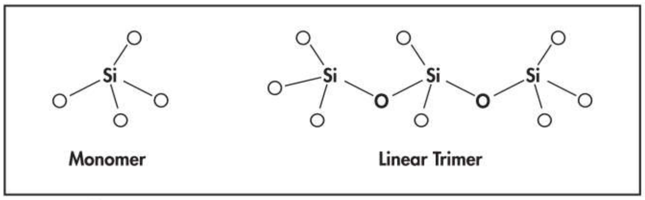
In addition to modifiers added deliberately, significant amounts of unintended unavoidable ions and species released from the minerals are also present in flotation pulps, and they can act as unintended (or inadvertent) modifiers. Even minerals themselves can act as unintended modifiers. The unavoidable ions and species formed in this process react with water, with each other, with other reagents forming complex ions and molecules, and colloidal and coarsely dispersed suspensions and precipitates. These species, in turn, adsorb on or adhere to air bubbles, thereby hindering bubble–particle attachment. These species also adsorb on, or react with, the mineral surfaces and change their surface compositions. The products and kinetics of these processes depend on the concentration of the interacting components, temperature, and, to a large degree, hydrodynamics. Temperature is not an important factor in most of sulfide flotation circuits (only small tonnage separation circuits like Cu-Mo separation may operate at higher temperatures) because the tonnages processed are too large and it would be cost-prohibitive to attempt to control temperature. However, because of seasonal variations, temperature does become a factor in many plants. Temperature is an important factor in many non-sulfide flotation circuits (e.g., fluorite, kaolin clay, and rare earth ores). The effect of unintended species in flotation is further complicated in plant circuits by large recirculating loads (common in sulfide flotation circuits; not so common in non-sulfide circuits) and recycled water (also most common in sulfide circuits; not so in non-sulfide flotation). Unavoidable species generated from minerals in the ore can have a wide range of effects on both efficiency and selectivity of separation via (a) interfering with collector adsorption on desirable minerals; (b) reducing flotation of targeted minerals; (c) promoting collector adsorption on, and flotation of, undesirable mineral(s); (d) changing froth characteristics; (e) changing pulp viscosity; and so on. One major effect is inadvertent activation of certain value minerals (Nagaraj and Brinen 1995, 1997; Smart et al. 1998; 2003; Stowe et al. 1995; Rao 2004). For example, inadvertent activation of sphalerite by Cu or Pb causes significant amounts of Zn misreporting to Pb and Cu concentrates. Other important examples are inadvertent Cu activation of pyrite in sulfide circuits and Ca activation of non-sulfide minerals in non-sulfide flotation circuits. Inadvertent activation is often difficult to predict, because it is strongly influenced by mineralogy and pulp conditions that exhibit significant variability in a plant. Indeed, one of the main functions of modifiers added deliberately (e.g., lime, soda ash, sodium silicate, polyacrylates, sodium sulfide) is to control the effects of inadvertent and unavoidable species.

Inorganic Modifiers

Action of inorganic modifiers. Inorganic compounds constitute the bulk of modifiers used in flotation. The material presented in this chapter characterizes only the intended

Table 9 Multiple modes of modifier action

	Mode of Action						
Modifier	**pH Regulator**	**E_p (pulp potential) Regulator**	**Depressant**	**Dispersant**	**Activator**	**Deactivator**	**Extender**
Lime	✓		✓	✓	✓		
NaOH	✓		✓	✓			
NH_4OH	✓						
Na_2CO_3	✓		✓	✓	✓	✓	
H_2SO_4	✓		✓		✓	✓	
HF			✓		✓	✓	
NaCN		✓	✓		✓	✓	
$Zn(CN)_2$			✓				
SO_2	✓	✓	✓		✓	✓	
NaMBS ($Na_2S_2O_5$)		✓	✓				
Na_2SO_3		✓	✓				
$Na_2S_2O_3$		✓	✓				
$NaSH/Na_2S$		✓	✓		✓	✓	
Nokes (P_2S_5+NaOH)		✓	✓				
$Na_4Fe(CN)_6$ or $K_4Fe(CN)_6$			✓				
H_2O_2		✓	✓		✓		
$KMnO_4$		✓	✓		✓		
$K_2Cr_2O_7$		✓	✓				
O_3		✓	✓				
Guar			✓				
Other gums			✓				
Carboxymethylcellulose			✓	✓			
Starch			✓				
Dextrin			✓				
Lignin sulfonates			✓	✓			
Tannin (quebracho)			✓	✓			
Na_3PO_4			✓	✓			
Synthetic polymers			✓	✓		✓	
Metal ions			✓		✓		
$CuSO_4$					✓		
$ZnSO_4$			✓				
$NiSO_4$			✓				
$Pb(NO_3)_2$					✓		
Ca^{2+}			✓		✓	✓	
Organic complexing reagents			✓			✓	
Sodium silicate			✓	✓	✓	✓	
Metal sols			✓				
Polyphosphates			✓	✓		✓	
Hydrocarbon oils							✓



Courtesy of PQ Corporation

Figure 3 Silicate structures

function. Inorganic modifiers exhibit a wide range of effects on flotation performance depending on circuit conditions, pulp chemistry, modifier dosage, and mineral composition of the ore. Inorganic modifiers also find use in treating recycled water that may harbor deleterious species. Functions, mode of action, and usage of various inorganic modifiers are shown in Table 10.

Acid and bases. Control of the pH of the pulp using appropriate acids and bases is one of the most significant methods for controlling interfacial chemistry, bulk-phase chemistry, and overall flotation selectivity and efficiency. Acids and bases often have multiple effects in flotation systems. Table 10 lists examples of how the major acids and bases are used in commercial flotation operations. Notably, hydrofluoric acid is quite hazardous and it has come under increasing scrutiny and regulatory pressure.

Salts of weak, medium-strength, and strong acids. The action of metal salts of different acids on flotation systems is even more varied than that of alkalis and acids, and a large number of these compounds is used as modifiers. The various commercially important salts used to modify flotation performance are listed in Table 10 with application examples. Many of these chemicals (e.g., NaSH, Na_2S, chromates, dichromates, permanganates, Na fluoride and Na fluorosilicate) present significant hazards and have come under increasing regulatory scrutiny.

Complexing and colloidal modifiers. In the selective flotation of sulfide and non-sulfide ores, inorganic modifiers are used, whose action is related not only to ionic adsorption and to simple ionic reactions but also to the formation of complex compounds and to the formation and action of colloidal sols. The commercially important ones are listed in Table 10, along with examples of their use.

Sodium and other metal silicates.[*] These form a family of commonly used multifunctional modifiers in flotation applications. Sodium silicate was introduced in the early days of flotation (1910–1920). There is extensive literature on silicate chemistry. Iler's (1979) book, *The Chemistry of Silica*, is a classic; and while it does include sections on soluble silicates, most of the very extensive book is not relevant for practitioners in flotation. There are more appropriate references pertaining to flotation (Falcone 1982; Marinakis and Shergold 1985; Qi et al. 1993; Yang et al. 2008).

Soluble silicates ($Na_2O \cdot xSiO_2$) contain three main components: silica, alkali, and water. All soluble silicates can be differentiated by the ratio SiO_2/Na_2O, which determines the physical and chemical properties of the product. Commercial sodium silicates are available with ratios of SiO_2 to Na_2O of 1.6–3.25.

Sodium silicate solutions contain numerous species of MW from 325–2,000 g/mole. Monomeric, oligomeric, and higher-MW linear polymeric arrangements of these structures exist in equilibrium in silicate solutions. At the molecular level, the fundamental building block of silicate species is SiO_4^{4-} anion, the silica tetrahedron consisting of the silicon atom at the center of an oxygen-cornered pyramid illustrated in Figure 3.

The mix of silicate anions in a soluble silicate solution is much more complex than a simple ratio may suggest, and this mix can substantially affect the properties and performance. In mineral pulps, soluble silicates undergo several simultaneous reactions to varying degrees depending on pH: (1) adsorption onto minerals, (2) complexation with metal ions, and (3) polymerization among silicates to form extended Si-O-Si networks in the form of sols, gels, and at very low pH as crystalline SiO_2.

Commercial sodium silicate with a ratio of 3.22 is most commonly used in mineral processing applications because of its high silica content and relatively low cost. It contains the highest amount of polymeric silica species. These polymeric species are highly charged and very reactive with polyvalent cations on mineral surfaces and in solution. Sodium silicates of lower ratios form a strongly alkaline pulp and will exhibit weaker depressing/dispersing abilities.

Various modes of action of Na silicate in mineral flotation are listed in Table 10.

Low-Molecular-Weight Organic Modifiers

Low-MW organic modifiers are used less frequently than inorganic modifiers, although their effect on the selectivity and efficacy in specific cases may be very significant. They often serve as complexing reagents or as depressants/dispersants. Applications of some selected modifiers are shown in Table 11.

Polymeric Modifiers

The types of polymeric modifiers in early use (pre-1950) were drawn from mostly naturally occurring water-soluble or water-dispersible polymers, such as starch, dextrin, glue, gelatin, gum arabic, and guar. Synthetic polymers were developed later.

These naturally derived polymers were used widely in depression of a variety of gangue minerals in sulfide and non-sulfide ore flotation, carbonaceous matter, molybdenite, and iron oxides (Nagaraj and Farinato 2016). The use of polysaccharides is reviewed in many articles (Mackenzie 1986; Pugh 1989). See Table 12 for more examples.

Naturally derived polymers tend to be nonspecific in their interaction with mineral surfaces (mainly via hydroxyl functional groups) and offer limited opportunities for incorporating mineral-specific functionalities. Synthetic polymers, which allow a wider range of functional groups and control of molecular architecture, can be designed to be more selective. Development of low-MW synthetic water-soluble polymers as modifiers dates back to the early 1950s. Aimone and Booth (1956) listed a large number of such polymers with various functional groups for flotation applications. The use of polyacrylates and hydrolyzed polyacrylamide as depressants and dispersants soon followed. While the use of polyacrylates for clays and slimes (Lin and Burdick 1987) increased, further

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[*] Information in this section was largely provided by PQ Corporation.

Table 10 Inorganic modifiers: Function, mode of action, effects, and uses

Modifier	Function/Mode of Action/Effects	Usage Examples*
Acid and bases	pH change leading to a change (beneficial or detrimental to flotation selectivity or efficiency) in (a) solubility of the mineral; (b) collector adsorption on value and/or gangue minerals; (c) ratio of individual ions and molecular forms of species (particularly weak acids, including ionic collectors) in the pulp; (d) formation of sparingly soluble colloidal precipitates (e.g., hydroxides, carbonates, and sulfates of multivalent metals, which can impact collector adsorption); (e) near-surface mineral composition, surface charge, and the attendant electrical double layer; (f) removal of mineral surface coatings that impede collector adsorption; (g) aggregation or de-aggregation of fine particles; (h) slime coating; (i) suspension stability and pulp viscosity, thereby altering gas dispersion and bubble–particle interactions; (j) water chemistry (bulk aqueous phase composition and dynamics thereof); and (k) froth characteristics, altering particle transport through froth. There is often a critical pH value above which flotation of many minerals is sharply depressed or promoted. Which result predominates depends on mineral composition in the pulp and the acid/base dosage.	**H_2SO_4 (sulfuric acid):** Surface scrubbing of sulfide minerals (e.g., pyrite, galena) to remove hydroxide and other hydrophilic coatings to improve flotation; increase floatability of sulfides (e.g., pyrite) that have been depressed with lime or cyanides; selective flotation of copper or bismuth sulfides (pH 2.5–4.5); depression of phosphate minerals in reverse flotation circuits; treatment of ilmenite to remove surface coatings; acid scrubbing of glass sands; sequential removal of impurities in feldspar and rare earth beneficiation.
		HF (hydrofluoric acid): Activation of beryl and selective depression of SiO_2 in flotation with anionic collectors; depression of spodumene, feldspar, and mica in flotation with anionic collectors; activation of feldspar and beryl flotation with cationic collectors; activation of ilmenite, chromite, spodumene, and zircon flotation with cationic collectors; depression of quartz, hematite, and pyrochlore flotation with cationic collectors; selective flotation of beryl from a bulk feldspar-beryl concentrate.
		H_3PO_4 (phosphoric acid): Depression of phosphates in the reverse flotation of carbonates from high-carbonate phosphate-dolomite-calcite ores.
		CaO, $Ca(OH)_2$, lime: Widely used in sulfide flotation (Cu, Cu-Mo, Cu-Au, Zn circuits, Ni circuits). Depressant for pyrite, marcasite and pyrrhotite; disperses many non-sulfide gangue minerals and slimes; precipitation of certain multivalent metal ions; pH control; pulp viscosity modifier; froth control; depression (at high lime dosages) of some copper minerals (e.g., enargite), galena, marmatite, and pentlandite; depression of silicates in flotation with cationic collectors; coagulation of fines.
		NaOH (sodium hydroxide): Preferred base when lime cannot be used (e.g., in fatty acid flotation); depression of certain sulfide minerals (e.g., pyrite, stibnite, galena, pyrrhotite); fluorite; niobium-bearing minerals; brookite; dispersion of slimes.
		Na_2CO_3 (sodium carbonate): Widely used in beneficiation of non-sulfide and polymetallic ores; dispersion and control of many problematic non-sulfide gangue minerals and slimes; sequestration of harmful multivalent metal ions; pH control; pulp viscosity modifier; depressant or activator in flotation with fatty acids; promotes spodumene flotation separation from beryl.
Salts of weak, medium-strength, and strong acids	Pulp potential regulation, sulfidization of surfaces of oxide or oxidized minerals (e.g., oxide copper minerals, tarnished sulfides); pH regulation; oxidation of mineral surface and sulfhydryl collectors; depression of sulfide minerals; sequestration and/or precipitation of harmful metal ions	**NaSH/Na_2S/Nokes (sodium thiophosphates; P_2S_5 + NaOH):** Activation of oxide copper minerals, tarnished sulfides at low concentrations; depression of collector-treated copper sulfide minerals, oxide copper minerals, iron sulfide minerals, cerussite, etc., at high concentrations; depression of oxides and silicates (quartz, feldspar, and micaceous shales) activated by iron cations; removal of non-sulfide slime coating and hydroxide coatings on sulfide minerals; enhancing flotation of molybdenite; precipitation of multivalent metal ions that may cause inadvertent activation (e.g., Cu^{2+} and Pb^{2+} ions); activation of cerussite, calamine, and smithsonite, especially at higher temperature.
		Na_2SO_3, SO_2, and other SxOy species: Used in combination with other modifiers (copper sulfate, zinc sulfate, NaCN, $Zn(CN)_2$); depress zinc and iron sulfides in polymetallic ore beneficiation; depression of galena in Cu-Pb separation; SO_2 with NaCN to depress copper sulfides; depression of pyrite in Cu circuits.
		$KCrO_4$ and $K_2Cr_2O_7$: Limited use due to environmental concerns. Depression of galena; selective flotation of copper sulfides from copper-lead bulk concentrate (in combination with Na sulfite); activates fluorite and selectively depresses barites to reduce fatty acid adsorption; calcite depression.
		$KMnO_4$: Limited use due to environmental concerns. Selectively depresses arsenopyrite (pH 5–7) and pyrrhotite (pH 7.5–9.0); depresses sphalerite and copper sulfides in the presence of galena; depresses bismuthinite in acid medium; depresses barites and, to a lesser extent, calcite and cassiterite when fatty acid collectors are used; activates fluorite; selective flotation of complex sulfide ores after activation with $CuSO_4$ and Na_2CO_3 ($KMnO_4$ depresses pyrrhotite and arsenopyrite); supplements Na silicate for depressing calcite in scheelite flotation in highly alkaline medium (pH ~11).

(continues)

Table 10 Inorganic modifiers: Function, mode of action, effects, and uses (continued)

Modifier	Function/Mode of Action/Effects	Usage Examples*
Salts of weak, medium-strength, and strong acids (continued)	Activation; depression	**NaF:** Activates ilmenite and fluorite flotation (by fatty acid); depresses apatite and some silicates; reacts with H_2SO_4 to produce HF in situ (e.g., activates ilmenite flotation from sulfide tailings with tall oil and kerosene).
		Na_2SiF_6: Depression of silicates and silica; depression of shale and sandstone; activation of tin and tungsten minerals and oxidized antimony ores; depression of zircon in the selective flotation of rutile-zircon concentrates by fatty acid and kerosene; depression of pyrochlore in the selective flotation from a pyrochlore-zircon concentrate by anionic collectors; direct flotation of martite in acid media (separation from iron-containing silicates, garnets, and others).
		$CuSO_4$ (copper sulfate): Activation of sphalerite, gold-bearing sulfide minerals; reverses the floatability of minerals depressed by cyanides (sphalerite, chalcopyrite, pyrite, and others).
		$CaCl_2$ (calcium chloride): Selective separation of fluorite from carbonate-fluorite ores; activates, at low concentration, oxide and silicate minerals in fatty acid flotation.
		$ZnSO_4$ (zinc sulfate): Depression of zinc sulfides in the selective flotation of Cu-Pb-Zn-Ag polymetallic ores (often in combination with cyanide and sulfoxy species).
		Iron salts ($FeSO_4$, $FeCl_3$) (not common): Depression of pyrite; slight depression of chalcopyrite and sphalerite and weak activation of galena in weakly acid media by $FeSO_4$; $FeSO_4$ depression of barite and wolframite; $FeCl_3$ depression of cassiterite and barite at low concentrations; forms Fe-Sols with sodium silicate (this is a more effective depressant).
		Aluminum salts ($Al_2(SO_4)_3$, $Al(NO_3)_3$) (not common): $Al_2(SO_4)_3$ depresses sphalerite (in combination with Na sulfite); depresses galena, pyrite, and sphalerite (in combination with Na thiosulfate); $Al_2(SO_4)_3$ depresses calcite and fluorite (in combination with Na silicate); activates barite; depresses fluorite and activates calcite at high pH; $Al(NO_3)_3$ aids in fluorite flotation (with fatty acid); stabilizes suspensions of barite.
Complexing and colloidal modifiers	Complexing compounds. Complexation results in soluble complexes, colloidal sols, gels, or precipitates. These can act as • Depressants by forming highly stable, hydrophilic complexes with metal sites on surfaces to prevent collector adsorption or remove adsorbed collector species, or by sequestering deleterious ions that might otherwise cause inadvertent activation; • Activators by removing hydrophilic coatings from mineral surfaces to enhance collector adsorption; and • Dispersants by increasing mineral surface charge in pulp, thereby increasing interparticle repulsions and reducing pulp viscosity, improving gangue drainage from froth (i.e., reduce entrainment) by modification of gangue surface charge and reducing froth viscosity.	**Cyanides (NaCN, $Na_4[Fe(CN)_6]$, $Na_2Zn(CN)_4$):** Depression of sulfides of zinc, iron, and nickel and, at high concentrations, also for copper sulfides (used only in alkaline media); Cu-Pb separation; ferrocyanide depression of secondary copper sulfides, chalcocite, bornite, and oxidized secondary copper sulfides in Cu-Mo separation.
		Na silicates ($Na_2O{\cdot}xSiO_2$): Widely used depressant and dispersant. Depressant and dispersant for quartz and silicate minerals (particularly clays) in phosphate, potash, tin, tungsten, iron ore (nonmagnetic taconite), and many other non-sulfide systems. Depressant for calcite, barite, and fluorite (activation at low Na silicate concentration); dispersant of slimes; in sulfide ore flotation, silicates are used in Cu-Mo separation circuits and in polymetallic flotation circuits. They are also used to reduce pulp viscosity when clays are present; improve selectivity by sequestering and complexing soluble metal cations (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+}) in the mineral pulp; depression of Fe-activated quartz (in combination with anionic collectors); used together with primary depressants such as polyacrylates, hexametaphosphate, starch, and carboxymethylcellulose; hydrophilic metal silicate formation, including metal sols, results in enhanced depression.
		Phosphates and polyphosphates (Na_2HPO_4, Na_3PO_4, $(NaPO_3)_6$, $Na_5P_3O_{10}$, $Na_4P_2O_7$): Common depressant/dispersant. Depression of phosphate minerals in reverse flotation of carbonates; depression of fluorite and calcite by disodium phosphate (pH dependent); selective flotation of fluorite from a complex fluorite-rare earth ore with a high calcite content; dispersion of clays, slimes, and other gangue in sulfide flotation systems including oxide Cu/Pb/Zn ores; soften hard water; selective fatty acid flotation of hydrargillite from kaolinite-hydrargillite bauxites (with fatty acids).

*These are based on either results published in the literature or observed in plant practice and are not an exhaustive list. Specific effects are strongly influenced by mineral composition of the ore and pulp chemistry. Exceptions may be expected.

Table 11 Small and low-molecular-weight organic modifiers

Reagent	Usage Examples*
Polyhydric organic acids and their salts[†] (oxalic, citric, tartaric, lactic)	• Prevent formation and growth of colloidal precipitates in flotation pulps; remove hydrophilic patches from value minerals to improve floatability (e.g., Fe hydroxyoxides from sulfide mineral surfaces using oxalic acid). • Depressants for iron-containing minerals in the flotation of cassiterite and of pyrochlore at low pH. • Depressants for barites in flotation of fluorite; depressants for fluorite and apatite; depressants for mica in sulfide flotation. • Depressants for silicates in flotation of lithium-containing minerals such as lepidolite and spodumene.
Tannins (quebracho)	• Depressant for calcite, silicates, and metal sulfides (mostly Zn, Fe, and Pb sulfides) in fluorite flotation, and for calcite in scheelite flotation. Condensed tannins such as quebracho are preferred to hydrolysable tannins such as tannic acid since they are more selective in the separation of calcite from fluorite. • Dispersion of slimes. • Tannins have been tested in the lab and plant as pyrite, pyrrhotite, sphalerite, galena, and Cu sulfide depressants in sulfide flotation, but commercial use in the plant is minor.
Lignins and sulfonated lignins	Use of lignin and sulfonated lignins has been investigated at lab, pilot, and plant level as gangue dispersants and depressants in the following systems: • Dispersants for non-sulfide gangue minerals (e.g., clays in Cu-Au flotation). • Depressants for pyrite (both activated and un-activated). Large dosages are required for efficient pyrite depression. Loss of selectivity at such high dosages limits their application in the plant. Loss of efficiency at high pH (>10.5). • Depressants for calcite and Mg silicates during flotation of sulfide ores. • Depressants for hematite in the amine flotation of silica from Fe oxide ores. • Depressant for calcite in the flotation of fluorite ores. Despite extensive testing, commercial use in the plant in both sulfide and non-sulfide flotation appears to be limited.
Naphthalene formaldehyde sulfonic acid	Depressant/dispersant for carbonaceous matter (graphitic and amorphous) and pyrite.
Polyamines (DETA, TETA)[‡]	DETA and TETA are used as pyrrhotite and pyrite depressants in Cu/Ni flotation.

*These are based on either results published in the literature or observed in plant practice and are not an exhaustive list. Specific effects are strongly influenced by mineral composition of the ore and pulp chemistry. Exceptions may be expected.

[†] Small organic molecules typically require high dosages as compared to polymeric modifiers. They often change the aquatic chemistry of the system because of build-up of various organic species that can impact the flotation of value minerals.

[‡] DETA = diethylenetriamine; TETA = triethylenetetramine.

Table 12 Polymeric modifiers

Reagent	Usage Examples
Polysaccharides	• Starch, dextrin, and guar are the most commonly used polysaccharides as depressants of a variety of minerals. • Starch is used as a depressant for molybdenite; high concentrations of starch depresses sulfides of lead, silver, and other metals (often used in conjunction with other modifiers such as SO_2, sulfoxy species). • Starch and causticized (hydrolyzed) starch depress graphite, carbonaceous minerals, micas, quartz, silicates, hematite, calcite, apatite, pyrochlore, aegirine, fluorite, barite, and others. • Starch can depress even collector-coated minerals. • Guar is primarily used as a depressant for talc. • Dextrin depresses calcite and more strongly depresses barite. • Dextrin depresses molybdenite, carbonaceous matter, and sericite. • Dextrin may depress spodumene and iron oxides in the flotation of mica, feldspar, and quartz with a cationic collector.
Cellulosics	• Carboxymethylcellulose (CMC) is used as a depressant or dispersant for Mg and Mg-Fe silicates (serpentines, talc, amphiboles, chlorite) in Ni, Ni-Cu, PGM ore flotation; also used as a dispersant for other slime-forming minerals in both sulfide and non-sulfide flotation. Depresses clays and other slimes in potash flotation with amines. • CMC depresses molybdenite.
Generic synthetic water soluble polymers (anionic, nonionic)	• High-MW polymeric flocculants may be used in the selective flotation of finely dispersed ores (e.g., potash beneficiation). • Polyacrylates and hydrolyzed polyacrylamides are used as dispersants and depressants for a large number of non-sulfide gangue minerals (e.g., kaolinite beneficiation); also used as pulp viscosity modifiers. • Polymers containing both carboxyl and sulfonate groups are excellent dispersants for a variety of silicate minerals, oxides, hydroxyoxides, and carbonates in sulfide and non-sulfide systems; they can sequester deleterious multivalent metal ions, reduce pulp viscosity, and control or eliminate slime coating. • Low-MW nonionic polymers of ethylene oxide and propylene oxide are used for depression and dispersion of Mg silicates in Ni ore flotation (especially in saline waters); froth control; improved P_2O_5 recovery in phosphate flotation (MgO rejection) (personal communication from Huntsman Corp.).
Designed-for-purpose synthetic water-soluble polymers (low MW; <100,000)	• Polymers with thiourea functionality: Depression of copper sulfides and pyrite in Cu-Mo separation from final bulk copper concentrates; separation of talc/carbon from sulfide minerals; depression of iron sulfides in base metal sulfide flotation; depression of sphalerite in Pb or Cu circuits. • Polymers with hydroxyl, carboxyl, and amide functionality: Depression of Mg silicates, such as talc, serpentines, and pyroxene in Ni and PGM ores; depression of pyrrhotite in Ni and Zn circuits; depression of carbonaceous matter and sphalerite in Pb circuits. • Polymers with hydroxy-carboxyl functionality: Depression of phosphate minerals in the reverse flotation of silica from phosphate ores; depression of iron oxides in reverse flotation of silica from iron ores; depression of slime-forming minerals (e.g., limonite, sericite, Mg silicates) in sulfide and non-sulfide systems.

Table 13 Analytical methods for chemical analysis of flotation reagents

Method	Principle	Capability/Advantages	Limitations
Spectrophotometry	Absorption of light in the UV region	Simple and fast technique, applicable to many collectors	Method is prone to interference, making it difficult to distinguish between different components in the sample. Sample preparation is needed to remove UV-absorbing solids.
Potentiometry	Measurement of changes in potential during titration of silver or copper nitrate, or copper sulfate with a flotation reagent such as xanthate	Ion-selective electrodes are applicable to low concentrations of collectors. Technique is selective if the correct type of electrode is used. Can easily be adapted to plant conditions (e.g., Xanthoprobe).	Not suitable for strong alkaline solutions such as those commonly found in flotation plants. Method is prone to interferences from sulfides, thiosulfates, carbonates, and thiocarbonates; different electrodes needed for different collectors.
Chromatography (HPLC)	Normal/reverse-phase chromatography or ion-interaction chromatography followed by UV detection	Possible to analyze many compounds at a time	Requires sample preparation (removal of solids by filtration).
Chromatography (capillary electrophoresis)	Separation method based on different electrophoretic movements of ions in an electric field	Possible to separate and detect different flotation collectors in process water	Different methods have to be developed for different collectors; requires sample preparation (filtration to remove solids).
Voltammetry	Concentration of chemical in solution is obtained by measuring current as potential is varied	Method is applicable to many types of collectors	The technique is tedious because of the need for sample preparation (N_2 purging, pH adjustment). Method does not differentiate between species in the sample.

Adapted from Lam 1999; Sihvonen 2012

development of synthetic polymers was rather slow until the 1980s when advances of commercial significance were made (Nagaraj et al. 1987; Nagaraj 2000; Bhambhani et al. 2014). As depressants, they offer many advantages over traditional ones (many of which are hazardous; e.g., NaSH, NaCN), such as ease of structural modification to suit different applications and ore variability, lower toxicity, lower transportation costs and storage hazards, better performance at lower dosage and lower treatment cost (exploiting the efficiency of a polymer molecule), ease of handling, and batch-to-batch consistency. For polymeric modifiers, structure–activity relationships take on added dimensions in terms of complexity and possibilities. In addition to changes in functional group, factors such as MW, degree of substitution, segment sequence, and distribution of functional groups become important. The mechanism of modifier action of these polymers is different from that of the non-polymeric modifiers such as sodium cyanide or sodium hydrosulfide; for example, polymeric modifiers generally do not alter and do not require any adjustment or control of pulp redox potentials.

Table 12 shows major functions and applications of natural and synthetic polymeric modifiers. Polymer selectivity and efficacy depends on dosage, mineralogy, water quality, processing conditions, and interactions with other chemicals in the system (added or inadvertent). Exceptions may be expected. Empirical ore flotation testing, preferably with either process water or simulated process water, is necessary. In general, polymeric modifiers require significantly lower doses than do inorganic or small organic modifiers to be effective; hence, they can have superior cost–performance benefits.

Chemical Analysis of Flotation Reagents in Plant Practice

Residual reagents (collectors, modifiers, and frothers) in process waters can have an impact on the flotation process and the environment if present in significant *relative* amounts in recycled and tailings waters. Analysis of flotation pulps for residual reagents or their degradation products is, therefore, of some value since it could be used as a diagnostic tool for control and optimization of the flotation process (e.g., dosage control), or as a way to monitor the composition of water discharged into the environment.

Various techniques for characterizing flotation reagents are given in Table 13. Offline techniques such as ultraviolet (UV) spectroscopy, high-pressure liquid chromatography (HPLC), voltammetry, titrimetry, and capillary electrophoresis have successfully been used to analyze flotation reagents in plant waters. Most of them are tedious (e.g., sample preparation) and slow, and do not offer real-time value to the operational improvement of the flotation process. However, they are very valuable in assessing environmental impact. Ion-selective electrodes (Chan et al. 1988; Bugajski and Gamsjger 1987; Cabrera et al. 2001) are extremely rapid and can be used in situ, but they are not sufficiently specific and robust in the presence of different reagents and mineral-derived species present in flotation pulps.

The best option would be online analyses that offer close to real-time, continuous, rapid, and reliable monitoring of flotation reagents. Various techniques have been developed and tested for this purpose (Hao et al. 2008; Luukkanen et al. 2003; Knight and Knights 2011; Sullivan and Woodcock 1973), but few have had sustained practical application. The online techniques successfully tested for plant flotation pulps are based on a simple arrangement involving a filter inserted in the flotation pulp and analysis of the filtered sample using UV spectrophotometry or titrimetry. Most attention has been given to xanthate in view of its wide usage in the industry. Automated online instruments such as Mintek's Xanthoprobe (Knight and Knights 2011) for determination of free xanthate in plants have shown success in plants using only xanthate.

Other categories of collectors (e.g., dithiophosphates, dithiocarbamates) as well as modifiers and frothers have received limited attention. Considering that combinations of collectors are often used to improve flotation performance and that many other types of species are present in plant flotation pulps, the greatest challenge is in developing a method that can distinguish between all these types of compounds. Another complexity in achieving this objective is interference from different species such as frothers and metal ions (Bushell and Malnarich 1956). Some of the interfering species are unknown and therefore cannot be corrected for. Even in systems involving only xanthate, formation of collector oxidation species and other concurrent reactions resulting in formation of disulfides and trithiocarbonates at the highly alkaline conditions prevalent in flotation pulps complicate chemical analysis of free xanthate by spectrophotometric methods (Pomianowski and Leja 1963). In this regard, chromatographic techniques, particularly those employing ion-interaction methods, are very attractive, though they are not suitable for online measurements. In the laboratory, it has been shown that a combination of online monitoring of flotation pulps by UV spectrophotometry and manual measurements by HPLC can be used to determine individual xanthates and xanthate decomposition products in one sample (Hao et al. 2000, 2008). Ion-interaction chromatographic techniques have also been successfully used to simultaneously analyze different collectors such as mercaptans, xanthates, dithiophosphates, dithiophosphinates, and dithiocarbamates (Barnes and Pohlandt-Watson 1988, 1993). However, their utility in industrial settings may be limited by the long time it takes to complete the analysis and the expertise needed to analyze the data.

Interest in the analysis of different flotation reagents is growing. Recent research has shown that capillary electrophoresis, a separation method based on differences in electrophoretic motilities of ions in an electric field, offers promise in lab and plant settings. Sihvonen (2012) described two capillary zone electrophoresis methods for analysis of flotation collectors from process waters. One method was able to separate and detect sodium di-isobutyl dithiophosphate and sodium di-isobutyl dithiophosphinate in pure water and flotation process water at detection limits <6.7 mg/L in less than 10 minutes. This method, however, was not able to quantify ethyl and isobutyl xanthates at acceptable detection limits. A separate method was developed for xanthates. The technique is yet to be fully developed for reliable usage in the plant.

All the available techniques are quite useful in assessing environmental impact of residual reagents in plant waters, though not for real-time in situ monitoring in plant circuits.

ENVIRONMENTAL, TOXICITY, AND REGULATORY ISSUES*

This section provides a very brief overview of environmental, toxicity, and regulatory issues that must be considered in the selection and use of flotation chemicals. These topics are broad and complex. Flotation practitioners should obtain the most-up-to-date information from reputable chemical suppliers and regulatory agencies, and, if available, consult their own company specialists (safety, hygiene, environmental, and regulatory).

Many regulations govern the use of flotation chemicals in plants, and these regulations vary from country to country. The following countries have implemented chemical control legislation for *new substances* (i.e., a chemical that is in either a totally new product or an existing product that is newly being introduced into the country in question) and have established national inventory lists of chemical entities that have been approved for manufacture and/or import: Australia (Australian Inventory of Chemical Substances), Canada (Domestic Substances List), China (Inventory of Existing Chemical Substances Produced or Imported in China), the European Union (EU Registration, Evaluation, Authorisation and Restriction of Chemicals, or REACH), Japan (Existing and New Chemical Substances, also known as METI, or Ministry of Economy, Trade and Industry), Korea (Korea Existing Chemicals List), the Philippines (Philippine Inventory of Chemicals and Chemical Substances), Taiwan, Switzerland, and the United States (Toxic Substances Control Act, or TSCA). Several other countries are contemplating initializing a chemical inventory. The landscape is rapidly changing and becoming more complex.

A product containing a component not on a country's inventory list cannot be manufactured, imported, or sold in that country without some type of registration or exemption. For the most part, regulations are for distinct chemical species. Therefore, if a product contains several new chemicals, each one would require regulatory approval, and, in some cases, the complex mixture, including impurities, would require regulatory approval. The legislation differs from country to country in terms of the type of tests (e.g., chemical and physical properties, mammalian toxicity, aquatic toxicity, mutagenicity, and environmental fate) required to add a chemical to a country's inventory. The details of registration requirements may depend on the volume of the chemical brought into the country and it may be the case that each importer/manufacturer must do their own registration.

For new chemical substances in the United States, submission to the U.S. Environmental Protection Agency (EPA) of a Premanufacture Notification (PMN) is the sole requirement for inclusion in the TSCA inventory. Currently, there are no mandatory toxicology testing requirements set forth by the EPA, but the EPA can require data after their initial review process. With future TSCA reform, this could change. As part of product stewardship initiatives and new product introduction processes, the reagent manufacturer should conduct a preliminary set of toxicity tests to assess the hazards of products so they can accurately warn downstream users of potential hazards of their product. The EU under REACH legislation, however, requires extensive testing based on production volumes to register a new or existing chemical. This process of conducting toxicity testing and filing a dossier can take 9–18 months to complete. Australia, Canada, China, Japan, and Korea also require extensive testing as part of their registration processes. The higher the production/import volume, the greater is the potential testing requirement. Typical testing costs, in U.S. dollars, range from $60,000 to $100,000 in the United States, $65,000 to $400,000 in the EU, and $50,000 to $220,000 in Canada. A typical Japanese METI registration can range from $280,000 to $430,000.

Meeting the testing requirements for Europe will satisfy many requirements for other countries because of the mutual acceptance of studies conducted by Organisation for Economic Co-operation and Development test guidelines. China's testing requirements are evolving but currently appear

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*Information in this section was produced with assistance from Amy Essenfeld of Solvay.

to be a combination of requirements for EU and Japan with some in-country testing requirements for aquatic toxicology studies. Efforts to harmonize registration requirements are continuing, but this effort will take many years to accomplish.

Flotation reagents cover a wide range of chemistries. Each chemical has its own set of hazards that should be reviewed prior to use. Chemical hazards are communicated in safety data sheets, or SDSs (formerly material safety data sheets, or MSDSs) supplied by the manufacturer. Plant health, safety and environment (HSE) specialists must (and indeed most do) thoroughly review the SDS of flotation reagents with consideration for use and assess their impact on (1) health and safety of operators, (2) surrounding communities, (3) air and water resources, (4) tailings ponds, and (5) the environment over a longer term. They are then responsible for ongoing training of plant personnel, especially operators who may be exposed to chemicals in the flotation plant. In cases where a facility does not have an HSE specialist, it is the responsibility of the practitioner to contact the chemical manufacturer to understand the hazards and then implement the appropriate safety, protection, and environmental measures. Although an SDS provides valuable information, it may not have information pertaining to the fate of a flotation reagent in use (i.e., from the arrival of the chemical in the plant to its fate during processing and afterward) including potential hazards of any degradation products and chemicals that may be present in the dispatched concentrates. Good sources for some of this additional information are reputable chemical manufacturers, many of whom have capabilities to conduct life-cycle analyses.

Attempts have been made to develop ranking schemes that more completely assess the HSE characteristics of a chemical, taking into account its manufacture, use, and ultimate fate through an industrial process. One example is the attempt to develop a Greenness Index by Shen et al. (2016a); however, this attempt is currently incomplete and was thwarted by the paucity of sufficient information on the fate of flotation reagents during use. This is an indication of the complexity of such a holistic analysis.

The importance of assessing a chemical through its use cycle in addition to its inherent chemical properties may be illustrated for the case of xanthates. Although the SDS for solid xanthate does not indicate any extreme hazard (the suggested U.S. Department of Transportation shipping label phrase is “spontaneously combustible“), it is known to hydrolyze when exposed to moisture or added to aqueous solutions and flotation pulps to continually generate toxic species such as carbon disulfide (CS_2) and carbonyl sulfide (COS). These species can accumulate in the flotation plants during use and can thereby present a significant HSE hazard. Potential health impacts can arise from these hazardous vapors accumulating in enclosed infrastructures and causing chronic operator exposure to these decomposition products. The permissible exposure limit (PEL) for CS_2 is 20 ppm (8-hour time-weighted average, or TWA) according to U.S. OSHA (Occupational Safety and Health Administration) as of this writing. The CS_2 PEL recommended by California OSHA is set even lower, at 1 ppm (OSHA 2017), and similarly in Canada.

Until recently, there was no study of xanthate decomposition in ore pulps under flotation conditions. Shen et al. (2016b) studied the fate of xanthate decomposition under laboratory conditions representative of flotation in ore pulps in a batch mode; however, this has not yet been extended to a continuous operation simulating plant practice, nor has it been extended to other flotation reagents.

In recent years, many countries have adopted a more harmonized way of classifying products and communicating their hazards. This Globally Harmonized System (GHS) has, unfortunately, not been adopted with the same requirements by all countries. Consequently, there are still some differences between countries, though there is now better alignment than in the past. The GHS uses standardized pictograms to alert people to the type and hazard level of a product.

These hazards are provided by the manufacturer in Section 2 of the GHS SDS. This section should be reviewed carefully prior to handling and storing the product. Special attention must be given to the following sections in the SDS:

- Section 3 (hazardous substances)
- Section 7 (handling instructions)
- Section 8 (personal protective equipment)
- Section 10 (stability and reactivity information)

The supplier should provide an overview of the product hazards and safe handling.

Sulfur-based reagents (mostly collectors and modifiers used in sulfide flotation) have the potential to present traces of hazardous sulfur-containing vapors such as carbon disulfide, carbonyl sulfide, and hydrogen sulfide in the head spaces of closed containers. These are typically either present in the reagent from manufacturing or are degradation products of the reagents after manufacture. It is important to monitor the levels of these vapors when the containers are opened to ensure that worker exposure is below safe levels. The PEL is often given as a TWA concentration of a chemical to which a person working an 8-hour shift can be exposed without suffering ill effects. The odor of many sulfur-containing compounds can often be detected at concentrations far below the PEL. The odor threshold of a compound is the lowest concentration that is perceivable by the human sense of smell. Smelling something offensive does not necessarily mean the PEL has been exceeded; however, it is always prudent to quantify potentially hazardous vapor concentrations and to evaluate exposure using direct measurement methods. It is important to note whether the odor threshold for a particular hazardous species is above or below its PEL value. Hazardous species concentrations must be kept below the established PELs in the workplace; adequate ventilation must be maintained. The PEL values for some common odiferous species are shown in Table 14.

REAGENT SELECTION AND OPTIMIZATION

Up to this point, a detailed account of flotation reagents and flotation chemistry for both sulfide and non-sulfide ore systems has been presented. This information coupled with the material later in Tables 17 and 18 provide the foundation for reagent selection and optimization. Additional details for specific systems can be found in the literature recommended throughout this chapter. In this section, the focus is on potential problems and pitfalls encountered in reagent selection and optimization, and presentation of a more holistic approach to dealing with these issues in general.

Reagent selection has two connotations: (1) selecting a single flotation reagent (e.g., a collector or frother or modifier)

Table 14 Odor thresholds and permissible exposure limits for some common odor compounds

Odor Compound (perceived odor)	Odor Threshold	Permissible Exposure Limit*
Carbon disulfide (foul sulfurous odor)	0.1–0.2 ppm†	OSHA PEL: 20 ppm TWA, 30 ppm ceiling ACGIH (TLV): skin, 1 ppm TWA
Hydrogen sulfide (rotten eggs)	0.005 ppm	OSHA PEL: 20 ppm ceiling ACGIH (TLV): 5 ppm STEL, 1 ppm TWA
Carbonyl sulfide (foul sulfurous odor)	0.05 ppm	ACGIH (TLV): 5 ppm TWA

*ACGIH = American Conference of Governmental Industrial Hygienists; OSHA = Occupational Safety and Health Administration; STEL = short-term exposure limit; TLV = threshold limit value; TWA = time-weighted average

†ppm = parts of vapor or gas per million parts of contaminated air by volume at 25°C and 760 torr.

or (2) a reagent scheme (i.e., type and dosage of collector, frother, modifier; pH; reagent preparation and conditioning; addition points and sequence). Each of these different meanings can be either for an existing operating plant (brownfield operation) for current ores being processed or for new/future ore types, or for a new mine/plant/project (greenfield project). The main difference is the level of uncertainty and unknowns—typically greenfield projects having more uncertainty and less constraints. Choice of a reagent or reagent scheme is intimately linked with mineralogy, plant metallurgical and economic constraints and objectives, mine plan, environmental factors, and flow sheet or circuit design. For some ore types, the choice of a reagent scheme may dictate a particular flow sheet, and vice versa. Examples include primary Au ores, polymetallic ores, Ni ores, and many non-sulfide ore systems. The presence of carbonaceous matter or certain penalty elements in primary gold ores may influence whether one changes the reagent choice or the flow sheet (e.g., preflotation or depression of carbonaceous matter). In polymetallic ores, reagent selection and flow-sheet design would depend on whether sequential or bulk flotation of Cu and Pb is chosen. In phosphate/carbonate ores, reagent selection and flow-sheet design depend on whether phosphate or carbonate is floated.

Reagent optimization has many connotations as well. To the plant metallurgists, for example, it may mean working with the reagent currently in use to find conditions (e.g., dosages, addition points) that provide *optimum* performance with respect to certain target metallurgical goals (e.g., improved recovery/grade, cost-effectiveness, improved HSE aspects). Or it may mean searching the market for an alternative reagent that provides performance better than the one currently in use. For a greenfield project, reagent optimization is typically not an important requirement given the uncertainties, limited number of drill-core samples available, and the absence of a plant to evaluate performance. To the chemical supplier, reagent optimization may mean modification of existing, or designing new, structures to provide reagents that perform better (for a given application, e.g., copper flotation) than currently marketed reagents, not just in any particular plant but across all plants in the industry. The ultimate goal is a robust solution to the needs in the dynamic plant system with all its variability. Although laboratory testing is an integral part of the process of optimization, its goal is merely to identify *potential* solutions, problems, and benefits. *True optimization occurs in the plant and not in the laboratory*.

The main driving factors in an operating plant include economics, value creation (maximizing cash flow within safety and environmental constraints), regulatory pressure, health, and safety. Reagent selection and optimization are intimately linked with each of these factors.

For a given separation problem (greenfield or brownfield), at first glance, the pool of reagent classes—and members within each class—available for selection may appear to be large, bewildering, complicated, and hopeless, especially for practitioners new to flotation. However, this is certainly not the case. This is partly the result of the evolutionary nature of reagent development over the decades. But more importantly, given the complexity and apparent idiosyncratic nature of the flotation system, a particular reagent class or a very specific member or homologue is required to produce the optimum results for the separation and ore type in question—the reasons for which are difficult to fully understand. General guidelines are available, including this chapter, for reagent selection in the form of an accumulated knowledge base: (1) in reagent developers' handbooks and product literature (e.g., the *Mining Chemicals Handbook* [Cytec Industries 2010]); (2) many useful articles describing plant practice in trade journals, conference proceedings, operators' forums; (3) expertise that exists in consulting/testing labs; and (4) experiential knowledge of metallurgists. There is also excellent literature on flotation chemistry. All these resources serve to establish a starting point and to narrow the selection for a given application; however, the metallurgist must still use additional criteria to refine the selection to a manageable level to move to the laboratory or plant testing phase where the selected reagents or schemes are properly evaluated and optimized to meet metallurgical and economic objectives. The major challenge in reagent selection and optimization is, therefore, not related to a lack of literature on the subject of reagent chemistry or selection but is one of incorporating the knowledge embodied in that literature to underpin an informed *approach* to reagent selection and optimization.

Problems and pitfalls are encountered when a reductionist and informal approach is applied to the two critical tasks—applying additional criteria (e.g., mineralogy, water chemistry, process variability) to refine the selection, and the design and execution of a laboratory or plant program. Flotation systems are complex, and problems in complex systems invariably have multiple solutions, each with its own degree of desirability. Even an arbitrary process of reagent (or reagent scheme) selection and evaluation will provide *a* solution to the separation problem in question (either in the lab or plant). However, such a solution may not be sufficiently robust or optimal (i.e., the selected reagent [or scheme] will have a narrow, unoptimized window of performance and may only be a temporary fix). The lack of reagent robustness with respect to system variability may not even be recognized if reagent performance is overwhelmed by the inherent variability in the system. A rigorous, statistical analysis of plant performance is needed to discern significant changes in plant performance outside of random noise or auto-correlated plant variations (Bruey 1999; Napier-Munn 2014; Napier-Munn and Meyer 1999). There is also the danger of a false positive (an inferior reagent or scheme yielding apparent improvement, leading to a mistaken conclusion that the reagent is superior) or a false negative (a superior reagent or scheme yielding apparent poorer performance, leading to a mistaken conclusion that there is deficiency in the reagent)—all due to improper design and execution of lab and/or plant testing. Even when the best reagent is developed for an unmet need in the industry, it is deemed a failure if we fail to apply it properly on the large scale. This issue becomes acute when one considers the high overall cost ($10 million or more from concept to commercialization) and the long time required (5–10 years) to develop and implement new reagents and technology. Compounding this problem is the exponential growth in environmental regulations and the high up-front cost of regulatory registration for new chemicals. Substantial improvements in operation effectiveness and value creation can be achieved at relatively low cost/performance ratios when optimal flotation chemicals are employed. A reductionist and informal approach is very costly in the long run and adds little to our knowledge base.

These issues are well documented in the literature (Nagaraj 1994, 2005; Cappuccitti 1994; Malhotra 1994; Klimpel 1994; Nagaraj and Bruey 2003; Nagaraj and Farinato 2016). These authors noted numerous reasons for the unfortunate prevalence of reductionist and informal approach to reagent selection and optimization over the past few decades.

Important factors that dictate reagent selection and trade-offs are listed in Table 15.

Factors grouped under constraints in Table 15 appear to be relatively straightforward; however, they can sometimes have an overriding impact on reagent selection. For example, a reagent selected on the basis of its superior metallurgical performance may be rejected for any of several possible reasons:

- Its odor is objectionable.
- It was not registered for use in the country where the plant is located.
- It might be perceived to present environmental problems.
- Its unit price is perceived to be unacceptable though the overall treatment cost would have been significantly lower.

Technical factors (see Table 15) present the greatest challenge in reagent selection, because many of these are difficult to fully assess in the preliminary reagent screening phase prior to laboratory evaluation. Consequently, a combination of available knowledge base, experience, and empirical diagnostic laboratory testing is used in an iterative process to assess the impact of the technical factors in reagent selection. The objective is to reduce the number of potential reagents and conditions that need to be evaluated in the laboratory. A holistic approach using highly efficient experimental designs and rigorous data analysis greatly facilitates the reagent selection and evaluation process and the chances of arriving at a robust solution rapidly.

The schematic shown in Figure 4 represents an expanded holistic view of the flotation system, especially of particular importance to reagent selection and optimization, depicting trade-offs as additional triangles. The expanded view of chemical factors reveals the flotation reagent triangle interacting with mineralogy (ore types). Only the chemical factors are expanded. The rationale is that much of the reagent selection process occurs in the laboratory stage where a plant's physical and operational factors are difficult to simulate. These factors are necessarily included when the reagent, identified in the laboratory, is taken to the plant. The resulting tetrahedron forms the basis for reagent selection and evaluation, in combination with triangles depicted for best practices, plant needs, and knowledge base—all emphasizing trade-offs.

A rational, holistic process comprising four critical phases is schematically represented in Figure 5. Although these four phases proceed in a logical sequence, they are indeed highly iterative. The discovery and definition phase provides all the necessary information for reagent selection and sets the objectives, goals, and success criteria. The reagent selection phase then begins with preliminary screening of available reagents using available knowledge base and expertise (e.g., of the reagent developer) to arrive at a subset of reagents that meet the requirements established in the discovery and definition phase. The selected reagents can then be screened in the laboratory by an iterative process. Historically, the preliminary screening phase has been rather simplistic and flawed as it involved merely selecting representative candidates from several different families, and essentially ignoring other important reagents in the circuit and operational variables. For example, if the objective is to screen collectors for a Cu ore, the candidate products might be xanthate, dithiophosphate, and thionocarbamates. These will then be evaluated one at a time while keeping all other reagents and conditions constant. This approach is used even for evaluating other variables such as pH, p80, ore type, and so forth. The erroneous assumption in this one-reagent-at-a-time or one-factor-at-a-time approach is that reagents (or variables) perform independently of one another.

A holistic approach for reagent selection is based on considering more than just the chemistry of one reagent in isolation or more than just one type of reagent for a given mineralogy. In fact, all the chemical and operational factors should be considered simultaneously. A combination of the technical factors, constraints, and issues delineated in Tables 15 and 16 must be considered to narrow down the candidates into a manageable subset for lab and plant testing, and optimization in plant use.

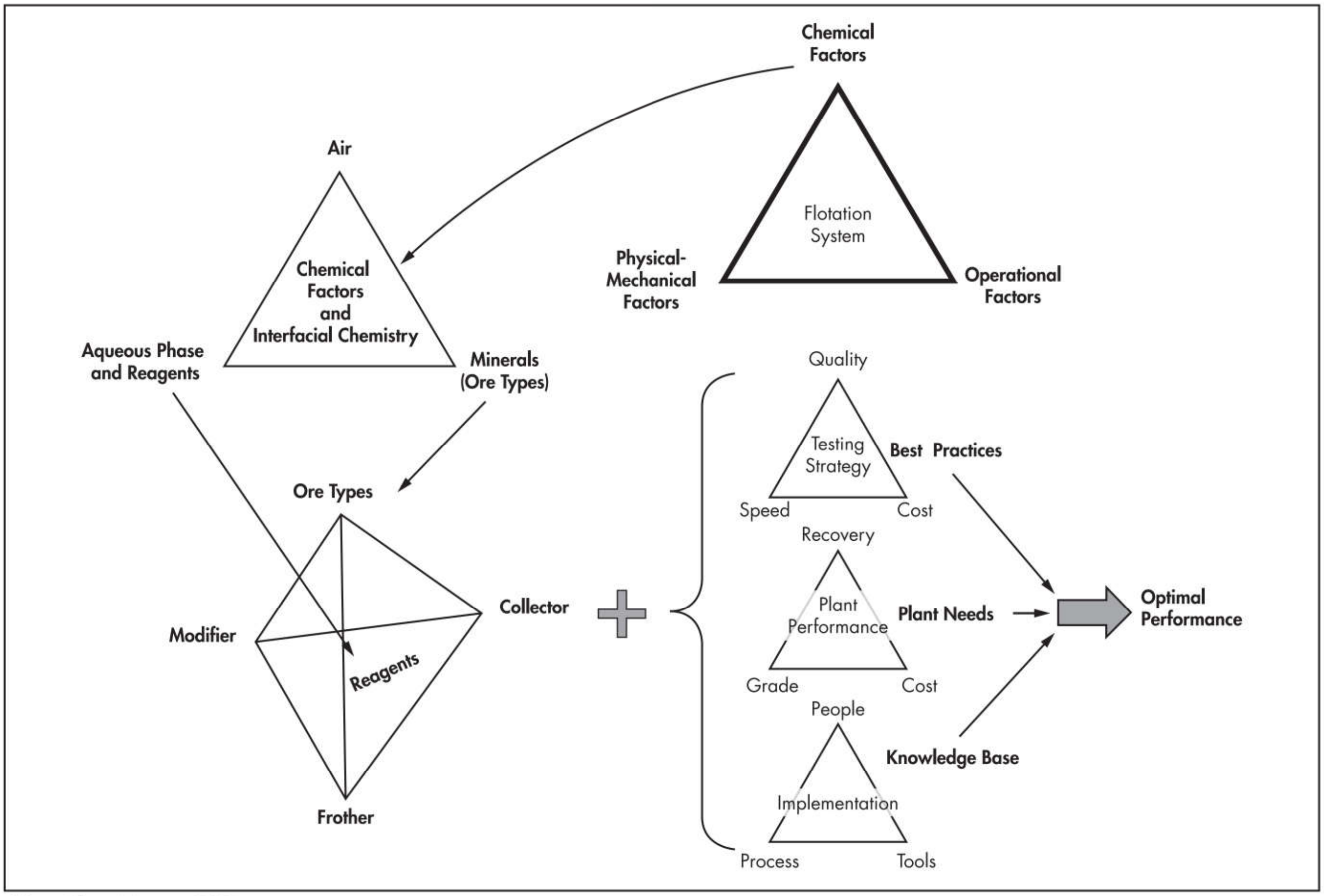
Rule-based expert systems for reagent selection have been developed more recently (developed by Cytec Industries in the early 2000s and mentioned by Franzidis 2005). These systems incorporate all the elements of the holistic approach, namely, definition of mineralogy and plant needs, reagent selection, and laboratory and plant best practices.

Collector selection is usually viewed as being easier than modifier and frother selection. However, even though there is

Table 15 Technical factors and constraints

Technical Factors	Constraints
Reagent chemistry	Reagent toxicology registrations
Ore types, mineralogy, and mineral chemistry	Handling
	Logistics
Frothing characteristics	Toxicity and environmental issues
Water chemistry and gangue minerals	Odor
Reagent stability (both short term and long term)	Manufacture
	Cost
Particle size distribution	Strategic fit
Downstream effects	
Co-value minerals recovery	
Plant circuit, process conditions, plant constraints	
Compatibility with other reagents	

Adapted from Nagaraj 2005



Adapted from Nagaraj 2005

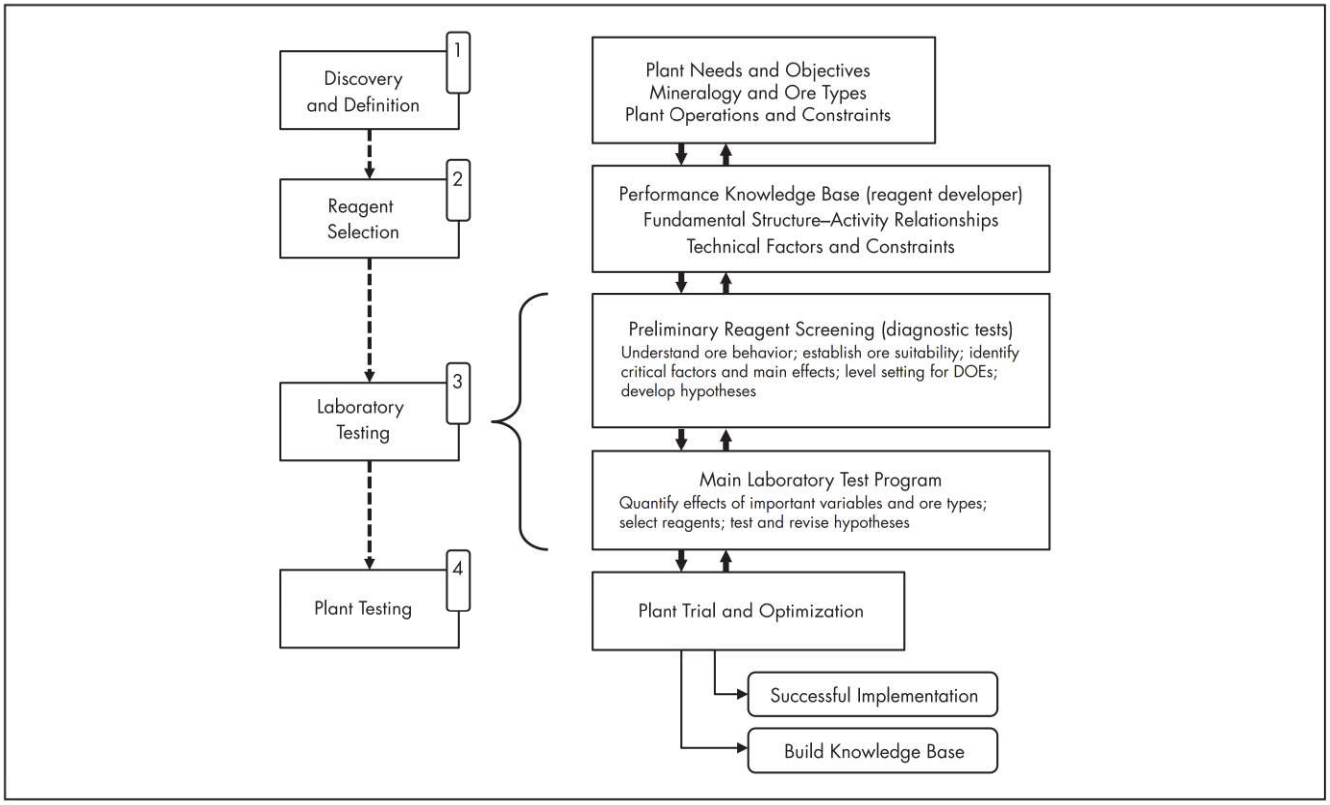
Figure 4 Expanded holistic view of the flotation system in reagent selection and optimization

a greater body of literature on collectors relative to modifiers and frothers, such collector literature remains slanted toward a rather narrow set of conventional chemicals (e.g., xanthate/MIBC/lime for a sulfide ore; fatty acid/soda ash for a nonsulfide ore). This effectively results in a narrowed set of options, often leading to suboptimization with respect to chemical selection. Nevertheless, general guidelines are available for all classes of flotation reagents, and these can form the basis of selection for a given application (e.g., chemical supplier handbooks and technical data sheets).

The available pool of reagents is large for collectors and modifiers. In contrast, the choice of a frother is limited to two main classes of compounds in terms of fundamental chemistry. Frequently, formulations are used to fine-tune a frother for a given specific application. Consequently, frother selection is invariably based on empirical testing, most often in the plant. Laboratory evaluation of frothers is generally (though somewhat inaccurately) considered to be inadequate. One reason is that the froth zone in a plant operation is very dynamic, and its properties are variable and strongly influenced by mineralogy and physical, operational, and chemical factors. Based on an extensive survey of plant usage of frothers, Booth and Freyberger noted in 1962 that "the same frother may be used in different plants in a given geographical area, but treating quite dissimilar ore types; conversely, different frothers may be used by plants treating almost the same ore types and similar plant conditions." This finding is valid even today, and many examples can be found for frother selections that are not based solely on a single visible attribute or a specific property or a single metallurgical response. Nevertheless, laboratory testing, when conducted properly (using a multivariate approach), can still be useful for an empirical ranking of frothers and for assessing their potential benefits and problems in a plant circuit.

Initial selection of a frother for any particular flotation operation should be contingent upon how closely a product fulfills the basic requirements in terms of several "appearance attributes," such as froth volume, bubble size, texture, stability, persistence (down the bank of cells), gangue and water carryover, mineral loading (carrying capacity), and froth mobility. Numerous qualitative descriptors (listed previously) are used in the plants. In this initial selection stage, the same technical factors and constraints that were shown in Table 15 are used. In any case, frother selection must be adequate to meet or exceed metallurgical targets. Currently, there is no reliable (i.e., predictive) and robust frother evaluation protocol for *practical ore flotation* in the published literature, although many methods are described for two-phase foams.

Selection and evaluation (either in the lab or plant) of modifiers are far more challenging than for collectors and



Adapted from Nagaraj 2005

Figure 5 Rational process for reagent selection and optimization

frothers. Many of the complex interactions and effects of modifiers are evident only in real flotation pulps and cannot be simulated in simple model systems such as single-mineral systems. Sometimes even laboratory ore flotation systems fall short of capturing effects of modifiers observed in plant circuits where the variability in mineralogy and operating conditions have a significant impact. Thus, effects observed in model systems used in laboratory investigation can be quite misleading. Single-mineral (or other model) systems do not capture the complexity and the dynamics of these interactions. Additionally, model system studies are conducted in the absence of other reagents (collectors and frothers). Consequently, results from such fundamental studies do not translate well to practical ore flotation. Thus, much of the published literature based on model systems is not relevant to modifier selection and optimization. They may, at best, provide some insights and concepts that could be tested in ore systems. For example, single-mineral studies may indicate that when lime is used as the modifier, adsorption of Ca^{2+} ions (or other metal ions) on sulfide particles, such as molybdenite or pyrite, may occur, resulting in depression of these minerals (Castro and Bobadilla 1995; Raghavan and Hsu 1984). However, ore flotation data and plant data do not seem to support results from single-mineral model system studies. Nevertheless, the belief that Ca ions depress MoS_2 and pyrite is quite prevalent.

General guidelines for modifier selection and evaluation were discussed earlier in this chapter, and numerous references are given there for additional information. As noted previously, mineral aquatic chemistry in flotation systems is complex and dynamic. Furthermore, flotation reagents work in concert, not independently of one another. In some systems, a change in collector type may impact selection of a modifier, or vice versa. Modifier function and the expected performance benefits are also highly dependent on pulp chemistry conditions and mineralogy—gangue minerals have a strong influence on modifier performance. In sulfide flotation systems, for example, certain non-sulfide gangue minerals—notably, clays, altered silicates (especially those of Mg-Fe), carbonates (e.g., calcite, dolomite, siderite), and hydroxyoxides (e.g., goethite, limonite)—can have severe adverse effects on both value minerals recovery and concentrate grade (Patra et al. 2012a, 2012b, 2014; Vasudevan et al. 2011, 2012; Farrokhpay 2012; Ndlovu et al. 2013; Zhang and Peng 2015; Cruz et al. 2013, 2015).

Prior to any selection and evaluation of modifiers, it is crucial to first diagnose the problems causing poor separation efficiency and selectivity. This is best done in ore flotation tests. For example, in a Cu-Mo-Au ore, the problem could be with concentrate grade, recovery of Cu/Au/Mo, or both. The root cause of the problem(s) could be (1) wrong collector, pH, or frother; (2) entrapment/entrainment of non-sulfide gangue (NSG) minerals; (3) hydrophobic NSG (e.g., C or talc); (4) NSG that increases pulp viscosity (e.g., high-aspect-ratio gangue); (5) sulfide gangue (e.g., pyrite); (6) slime (fine fraction) minerals (e.g., clays, hydroxyoxides); or (7) deleterious aqueous species derived from minerals, process water, or added chemicals (e.g., lime). Diagnosing the problem(s) can be accomplished via well-designed ore flotation testing, qualitative and quantitative mineralogy (especially the fine

Table 16 Factors in reagent selection and plant use

Factor	Issue	Solution
Cost	Perceived high cost of the proposed alternative reagent	Focus on delivered value, not the unit cost of the reagent.
Choice of reagent and application scheme	Not based on realistic needs, goals, commercial and technical viability, but based on personal experience, gut feeling, anecdotes.	Focus on "total system"; holistic selection criteria.
	Narrow focus on limited set of collectors and modifiers. Inadequate use of scientific method and existing knowledge base.	Options considered should be broadened to include the wider palette of reagents, and consideration of the inherent complexity of practical systems must be taken into account.
Application knowledge	Improper selection and use of reagents.	Use published and experiential knowledge and incorporate it into reagent selection and application.
Setting lab and plant test objectives	Testing objectives that do not meet or are inconsistent with plant needs and constraints (equipment, circuit configuration, etc.). Not all plant problems are solvable by chemical means.	Plant needs, constraints, and objectives must be clearly understood, defined, and agreed upon before a single test is run or a solution is recommended.
Lab and plant test execution	Inadequate or improper testing yielding misleading information regarding the efficacy of a flotation reagent, and leading to expensive failures in plant. The lack of standardization of laboratory flotation testing best practices and statistical tools (e.g., experimental design).	Use data-driven decision making. Employ well-designed testing plans based on sound hypotheses and a holistic approach, which account for interactions among the important factors.
Health, safety, and environmental (HSE) assessment	Failure to quantify HSE benefits of reagents leading to lopsided analyses and lost opportunities for value creation (e.g., focusing only on reagent unit cost and not accounting for HSE benefits).	Monetize the impact of environmental regulations and HSE aspects; then act to mitigate risk, and protect employees and the environment.
Societal	Hazardous chemical risk reduction; sustainable natural resource development, and better legacy.	Conduct proper evaluation and monetization of safer, alternative chemicals and processes.
Return on investment (ROI)	Faulty ROI calculations due to a lack of proper analysis (e.g., basing ROI only on reagent unit cost; not considering co-value recovery, penalty element rejection, logistics and handling issues, downstream effects).	Base ROI calculations on a complete, holistic analysis of costs, benefits, and risks.
Industry adoption and valuation of technology	Lack of plant's willingness to (1) test and adopt new flotation reagents, (2) consider alternative conditions to accommodate the new chemistry, (3) completely assess the value of new technology.	Valuation of a technology should include cost–performance metrics over the complete life and use cycle of the materials, and the overall (holistic) benefits to the entire plant operation.
Education and expertise	Shortage of qualified metallurgists; declining availability of education in mineral processing.	Industry, government, and academe should work closely to promote mineral industry education.
Economic pressures	Pressure on plants to find ways to further cut costs when ore grades decline in order to be competitive in the new global economy.	Proper reagent selection is paramount. This allows maximal leveraging of chemical solutions to hedge against declining ore quality, especially given the fixed nature of plant equipment.

Adapted from Nagaraj 1994; Nagaraj and Ravishankar 2007

size fraction), water chemistry analysis, pulp viscosity, batch settling behavior, and a thorough understanding of the plant flow sheet including plant data analysis. This yields a more rational basis for modifier selection.

Once modifiers are selected, they must be evaluated via empirical testing using a holistic approach in which mineralogy, flotation reagents, and conditions are all considered simultaneously and all the technical factors and constraints are included in the screening phase.

The ultimate choice of any flotation reagent is invariably based on empirical testing in the laboratory followed by rigorous testing in the plant, and to a large extent on the overall or global performance of the reagent in the plant (i.e., not just in one small part of the whole plant circuit). Details of the laboratory testing and plant testing phases in the process of reagent optimization are discussed elsewhere (Nagaraj and Bruey 2003; Nagaraj 2005, 2008).

MAJOR INDUSTRIAL SEPARATIONS

Base Metal Sulfide and Precious Metal Ores

Many of the industrial separations from sulfide and precious metal ores require the separation of value sulfides from each other or the separation of value sulfides and precious metals from NSG. In each case, a specific reagent scheme is necessary to effect the separation and produce a salable flotation concentrate. In some ores, the occurrence of penalty minerals, oxidized or tarnished mineral surfaces, or carbonaceous matter (i.e., graphite and amorphous carbon) greatly influences the choice of reagents employed. Table 17 is a compilation of features of the major industrial separations for base metal sulfide and precious metal ores. The material in this table is based on plant practice and many other sources (loc. cit.).

Major Industrial Separations—Non-Sulfide Ores

Table 18 is a compilation of features of the major industrial non-sulfide mineral flotation separations. The material in this table is based on plant practice and many other sources, including Manser 1975; Aplan 1994; Arbiter and Williams 1980; Aplan and Fuerstenau 1962; Cytec Industries 2010; Coghill and Clemmer 1935; Davis 1985; Redeker and Bentzen 1986; Falconer and Crawford 1947; Falconer 1961; Gaudin and Glover 1928; Holme 1986; Houot 1983; Jones and Oblatt 1984; Malhotra and Riggs 1986; Somasundaran and Moudgil 1987; Mulukutla 1994; Miller et al. 2002; Fuerstenau 1962; and Fuerstenau et al. 2007.

Table 17 Main industrial separations: Sulfide minerals

Ore	Main Minerals	Desired Separation	Typical Reagent Scheme(s)
Copper	Chalcopyrite, chalcocite, digenite, covellite, bornite; pyrite, minor amounts of acid-soluble Cu minerals (ASCu)	High selectivity against pyrite	Lime is used to maintain pH range ~9–11 in the roughers, and ~11–12 in the cleaners to depress pyrite. Alkyl dithiophosphates, functionalized thionocarbamates, dithiophosphinates, and dialkyl thionocarbamates, and formulations thereof, are the primary collectors to achieve both recovery and selectivity. A xanthate in small dosages is used if necessary as a secondary or scavenger collector. Dialkyl dithiophosphinates are finding increasing use as Cu sulfide collectors because of their strong collecting power, high selectivity against iron sulfides, low frothing contribution, and fast kinetics at much lower dosages than other primary collectors. Sulfoxy compounds (e.g., sulfite, metabisulfite) and NaCN are sometimes used as pyrite depressants. Functionalized polymeric depressants are also used; they are safer and easier to use. Alcohol, polyglycols, and combinations thereof, are used for desired selectivity or better kinetics
		Selectivity against As and Sb minerals (penalty minerals)	Functionalized thionocarbamates in combination with short-chain dithiophosphates are commonly used. Dialkyl dithiophosphinates may offer better overall performance because of their selectivity against certain penalty element minerals.
		Acid circuit flotation (pH <6)	Sulfuric or sulfurous acids are commonly used as pH modifiers. Alkyl monothiophosphates, mercaptobenzothiazole, and dialkyl dithiocarbamates (often with dithiophosphates) are primary collectors. Very limited use of dialkyl xanthogen formate.
		Flotation of oxidized or tarnished ores	Mercaptobenzothiazole and dithiophosphate collectors are used in conjunction with xanthate. Small dosages of alkyl hydroxamic acids may be used to improve recovery of ASCu.
Copper-gold	Chalcopyrite, chalcocite, covellite, bornite, native gold (alloys), pyrite	Selectivity against iron sulfides: when gold is present in copper sulfides	The objective is to float Cu sulfides and Au values selectively but not float pyrite. Lime is used to provide high pH required for depression of non-gold-containing pyrite. NaCN and/or functionalized polymeric depressants for pyrite control may be used. Primary collectors include dialkyl dithiophosphinates, aryl and alkyl monothiophosphates, oily dithiocarbamate, dithiophosphates (especially short chain), and formulations thereof. Functionalized (sulfonate and carboxyl) polymeric dispersants or depressants are often used for slime control. Frothers include alcohols, glycols, and combinations. Difficult-to-float coarse gold normally recovered by centrifugal concentration or flash flotation. Any unrecovered gold in the tailings can be recovered by cyanidation depending on economics and mineralogy.
		When significant gold is present in pyrite	A bulk copper-gold-pyrite concentrate using the preceding reagent scheme is typically obtained in the pH range of 7–10 to avoid depression of gold-containing pyrite. Copper and gold are then recovered from the bulk concentrate by first cleaning it and then making separate Cu-Au and pyrite-Au concentrates by depressing pyrite at high pH.
		When gold is associated with oxide Cu minerals	Improved copper recovery can be obtained by combining hydroxamate-based collectors with the copper-gold collectors listed previously, and by sulfidization-flotation.
Copper-molybdenum	Chalcopyrite, chalcocite, covellite, bornite, molybdenite, pyrite	Bulk Cu-Mo flotation followed by Cu-Mo separation	Cu-Mo bulk flotation: Primary collectors include alkyl dithiophosphates, functionalized thionocarbamates, dithiophosphinates, and dialkyl thionocarbamates, and formulations thereof. Hydrocarbon oil, oily xanthate ester, oily dithiocarbamate, and functionalized thionocarbamate to enhance recovery of molybdenite and any gold values. Cu-Mo separation: Depression of Cu sulfides and pyrite using NaSH, Na_2S, Nokes, $(NH_4)_2S$, and floating molybdenite using hydrocarbon oil. NaCN is sometimes used to depress residual Cu sulfides and pyrite in the Mo cleaners. New functionalized polymeric depressants can replace 50%–90% of the hazardous inorganic depressants mentioned previously while improving the efficiency of the Cu-Mo separation. Formulations of alcohol-glycols with hydrocarbons are widely used frothers.
Primary gold (refractory ores)	Native gold, electrum, tellurides, sylvanite, petzite, auricupride, maldonite, and many others; several sulfide minerals	Bulk flotation to recover Au values and associated minor amount of sulfides	Bulk gold flotation is achieved by using a strong xanthate collector such as potassium amyl xanthate in combination with secondary collectors such as oily dithiocarbamate, short-chain alkyl dithiophosphates or dithiophosphinates and mercaptobenzothiazole. Gold in bulk concentrate is recovered by cyanidation (after roasting or pressure oxidation); Au in tails is recovered by cyanidation depending on economics. Strong alcohol/glycol frother blends are used to enhance coarse Au recovery.

(continues)

Table 17 Main industrial separations: Sulfide minerals (continued)

Ore	Main Minerals	Desired Separation	Typical Reagent Scheme(s)
Primary gold (refractory ores) (continued)		Flotation of gold associated with sulfide minerals (pyrite, pyrrhotite, arsenopyrite, arsenian pyrite, marcasite, enargite, tennantite and tetrahedrite, realgar/orpiment)	The objective is to float all sulfide and Au values (pH 4–10 depending on mineralogy). Strong collectors such as amyl xanthate along with dithiophosphinate, oily dithiocarbamate, aryl or alkyl monothiophosphate, mercaptobenzothiazole, and dithiophosphate are employed. The concentrate is then treated by cyanidation after roasting or pressure oxidation. A significant amount of xanthate can often be fully replaced by a combination of the other collectors. Cu- or Pb-activation is practiced for many ores to enhance flotation of gold carriers such as pyrite, arsenopyrite, arsenian-pyrite, and other sulfide minerals. Success of this practice depends on particular pulp conditions such as pH, E_p. When the ore contains low amounts of acid-consuming minerals, flotation is conducted in acid-circuits (pH 3–7) to enhance flotation of sulfide minerals. Mercaptobenzothiazole with di- and mono-thiophosphates are quite effective collectors.
		Ores containing problematic non-sulfide gangue minerals such as Mg silicates, clay minerals, hydroxyoxides, carbonaceous matter	One or more modifiers (dispersants or depressants) are added to improve selectivity. The choice of modifier depends on the type of non-sulfide gangue mineral, pulp conditions, and flow sheet. Selective rejection of nuisance carbonaceous matter can be achieved by (1) implementing a carbon prefloat using collector/frother formulations based on hydrocarbon oils or more effective specialty formulations to enhance recovery of slow-floating carbon (the carbon prefloat concentrate may be reprocessed to recover Au values), or (2) carbon depression and "blinding" using dextrin (sometimes with controlled dosage of dyes for efficient C depression).
		Tarnished ores and ores containing significant quantities of arsenopyrite	Copper sulfate is typically used to activate sulfides. Mercaptobenzothiazole with mono and dithiophosphates and oily dithiocarbamates enhance arsenopyrite and gold recovery. Concentrate is pretreated by roasting, biooxidation, or pressure oxidation prior to cyanidation. Tailings are treated by cyanidation if they contain sufficient gold.
Primary molybdenum	Molybdenite, minor amounts of sulfides of Cu, Fe, and Pb	Flotation to produce a high-grade Mo concentrate	Hydrocarbon oils are used as collectors to enhance the natural floatability of molybdenite. Xanthate esters and functionalized thionocarbamates serve as secondary collectors. Alcohol-based frothers are used to enhance flotation kinetics in rougher flotation. A strong glycol based frother is often used to carry the rougher concentrate through multiple cleaning stages. Sodium silicate and/or soda ash are used for slime and pH control. Sulfide gangue minerals are depressed with Nokes reagent or polymeric modifiers.
Lead	Galena, cerrusite, anglesite, plumbo-jarosite	Recovery from high-grade galena ores	Galena is best floated at natural or slightly alkaline pH (~8.5) as it is depressed by high OH^- concentrations; Na_2CO_3 rather than lime is used for pH control (though lime is used in some cases). Primary collectors are dithiophosphinate, ammonium aryl dithiophosphate, and ethyl or isopropyl xanthate. Formulated collectors are often used as partial or full replacement of xanthate.
		High selectivity against zinc and iron sulfides	Stage addition of dithiophosphinate or ammonium aryl dithiophosphate offer better selectivity than xanthates and improve Ag recovery. Cyanide is sometimes used to provide better selectivity against zinc and iron sulfides.
		Recovery of Pb from oxidized lead ores	For slightly tarnished ores, mercaptobenzothiazole with dithiophosphate is very effective in addition to a sulfidizing agent such as sodium sulfide. For highly oxidized ores, lead sulfide is first recovered using collectors mentioned previously; oxide Pb minerals are then recovered by sulfidization followed by flotation using same collectors.
Lead-zinc	Galena, cerrusite, anglesite, sphalerite, marmatite, smithsonite	Recovery of high-grade Pb and Zn concentrates and rejection of iron sulfides	General practice is Pb flotation followed by Zn flotation. Soda ash is normally used for pH control, ~8–10. In the Pb circuit, zinc minerals are depressed with $ZnSO_4$, Na_2SO_3, $Na_2S_2O_5$, NaCN, $Zn(CN)_2$, or combinations. Primary collectors for Pb are same as those mentioned previously. Aryl dithiophosphate appears to be selective when Zn is somewhat activated. $CuSO_4$ is used as an activator of Zn minerals in the Zn circuit. pH is typically in the range 10–12 for pyrite and pyrrhotite depression. Primary collectors in the Zn circuit are xanthates, thionocarbamates, short-chain dithiophosphates, and combinations thereof. Alcohol frothers are more common, often with controlled amounts of glycols.
		Rejection of gangue carbonaceous minerals, dolomite, or magnesite	Organic depressants such as lignin sulfonates, quebracho, dextrin, and nigrosine are commonly used in the lead and zinc circuits for depression of gangue minerals.

(continues)

Table 17 Main industrial separations: Sulfide minerals (continued)

Ore	Main Minerals	Desired Separation	Typical Reagent Scheme(s)
Copper-zinc	Copper sulfides, sphalerite, Ag values, minor galena	Differential flotation of copper sulfides from sphalerite and rejection of pyrite and pyrrhotite	Most common plant practice is sequential flotation: Selective Cu flotation (depressing Zn minerals) followed by $CuSO_4$ activation of Zn (depressing any pyrite). Lime or soda ash to control pH ~9–10.5; lower pH (~6–8) used in some plants (especially when SO_2 is used in Cu circuit to depress Zn and Fe sulfides). $ZnSO_4$, Na_2SO_3, $Na_2S_2O_5$, SO_2, NaCN, $Zn(CN)_2$, or combinations used to depress Zn and Fe sulfides. Primary collectors are dithiophosphinate, dithiophosphate, thionocarbamates, and xanthate, and combinations to maximize Cu/Ag recovery and selectivity. Alcohol-type frothers are common; glycols and combinations are also used. Primary collectors in Zn circuit are the same as described previously.
Copper-lead-zinc	Copper sulfides, galena, sphalerite, Ag values	Bulk Cu-Pb flotation (depress Zn and Fe sulfides), Cu-Pb separation, and Zn flotation	Cu-Pb flotation: Primary collectors are dithiophosphinate, aryl dithiophosphate, and xanthate; depressants for Zn and Fe sulfides same as described previously (see copper-zinc minerals). Cu-Pb separation is achieved by either selectively depressing Pb or Cu while floating the other, depending on Cu/Pb ratio, feed grades, and mineralogy. Pb depressants: Na_2SO_3, $Na_2S_2O_5$, SO_2, starch, and $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ (only if permitted). Cu depression (while floating Pb) is less common; achieved with NaCN; environmental issues with NaCN and potential risk of depressing Ag/Au values. $Zn(CN)_2$ is an alternative. Zn flotation after Cu-Pb bulk flotation is the same as listed previously.
		Sequential Cu, Pb, Zn flotation	This scheme requires the appropriate use of depressants ($ZnSO_4$, Na_2SO_3, $Na_2S_2O_5$, SO_2) for galena, sphalerite, and pyrite depressants during selective Cu flotation. Cu flotation: Very selective collectors, which are also poor galena collectors, such as the alkyl dithiophosphates or modified thionocarbamates are used to float Cu minerals. Pb flotation: Pulp is conditioned with cyanide to depress zinc minerals and activate Pb. Dithiophosphinates, ammonium salts of aryl dithiophosphates, and xanthate are used as collectors. Zinc minerals are floated next as described previously. Alcohol-type frothers are used in copper-lead-zinc separations for maximum selectivity.
Nickel (sulfide ores; lateritic ores are treated by hydrometallurgy)	Pentlandite, millerite, violarite, heazelwoodite, with varying amounts of pyrrhotite	Recovery of a high-grade nickel concentrate from nickel sulfide ores, rejection of mostly Mg silicates (talc and serpentines)	Xanthates are widely used collectors. Dithiocarbamate, dithiophosphinate, and dithiophosphate are used as secondary collectors. A significant amount of xanthate can be replaced by formulations based on alkyl dithiophosphates, functionalized thionocarbamates, dithiophosphinates, and dialkyl thionocarbamates while improving recoveries or selectivity. $CuSO_4$ activation may be used to enhance flotation of Ni minerals and pyrrhotite (if necessary). Rejection of Mg silicates is achieved with guar, carboxymethylcellulose (CMC), and functionalized polymers. Pyrrhotite depression (when necessary) is achieved with soda ash, DETA, and/or NaCN (if environmentally acceptable), sodium sulfite, and functionalized polymers (safer and relatively nonhazardous). Alcohol and alcohol/glycol blends are common.
Nickel-copper	Chalcopyrite, pentlandite, millerite, violarite, heazelwoodite, pyrrhotite	Sequential Cu, Ni flotation followed by Ni-Cu separation or bulk Cu-Ni flotation followed by Cu-Ni separation (choice dictated by Ni/Cu ratio)	Bulk Cu-Ni flotation: Primary collectors are xanthate in combination with dithiophosphinate, dithiocarbamate, and dithiophosphate. pH 7.5–9.5 (with soda ash or lime). Functionalized polymers may improve pyrrhotite rejection. Floated pyrrhotite is rejected after Cu-Ni separation. If pyrrhotite is a minor component, $CuSO_4$ activation may be used. Xanthates used in nickel-copper flotation can be replaced with certain formulations based on alkyl dithiophosphates, functionalized thionocarbamates, dithiophosphinates, and dialkyl thionocarbamates for increased recovery of metal values in the Ni-Cu bulk concentrate. Use of some formulations enables Cu-Ni flotation to be conducted under acidic conditions thereby improving recoveries. Talc and serpentines are depressed as described previously for nickel ores. Cu-Ni separation is achieved by depressing Ni minerals with lime (pH 11–12) and small amounts of cyanide (if permitted). Functionalized polymers, starch, dextrin may also be used.
Platinum group metals (PGMs)	PGM alloys, Au/Ag, PGM arsenides, tellurides, Cu, Ni, Fe sulfides	Bulk flotation of PGMs, copper and nickel sulfides	Xanthates (at high dosages) are primary collectors; dithiophosphates, dithiocarbamates, and small amounts of modified thionocarbamates and xanthate esters are secondary collectors. Guar, CMC, and functionalized polymers are depressants for talc and other Mg silicates. Weaker frothers are typical to ensure low mass pulls.

Table 18 Main industrial separations: Non-sulfide minerals

Ore	Main Value and Gangue Minerals	Desired Separation	Typical Reagent Scheme(s)
Barite	Barite and gangue minerals: fluorite, celestite, calcite, quartz, siderite, goethite, galena, sphalerite, and limonite	Recovery of high-grade barite	Sodium silicate is used as a pH modifier and slimes dispersant. Primary collectors are alkyl sulfates, petroleum sulfonates, or formulations. Collectors with high petroleum sulfonate content are particularly effective since they are tolerant to slimes. Partial replacement (~5%–20%) of petroleum sulfonate with alkyl sulfosuccinamate improves performance and circuit control.
		Selectivity against fluorite and calcite	Alkyl sulfosuccinamate as primary collector with moderate to high amounts of sodium silicate provides a high degree of selectivity against fluorite and calcite that cannot be obtained with petroleum sulfonates. Much lower dosages than with petroleum sulfonates.
Tin ores	Cassiterite with gangue minerals quartz, dolomite, siderite, Cu and Fe sulfides, tourmaline, wolframite, scheelite	Selectivity against gangue minerals	Flotation feed (gravity concentration tailings in most plants) is conditioned with sodium silicate, sodium fluoride, or sodium fluorosilicate as gangue depressants and/or dispersants. pH is then adjusted to 3–5 using H_2SO_4 to depress silicate minerals. If sulfides are present, they are removed using a xanthate, dithiophosphate, mercaptobenzothiazole. $CuSO_4$ may be used to activate sulfides. Tailings from the sulfide flotation stage are treated with cassiterite collectors. Styrene phosphonic acid (SPA), alkyl sulfosuccinamates, or combinations are the primary collectors. Use of arsonic acids is limited because of environmental restrictions. SPA is preferred for finely disseminated cassiterite ores. Phosphoric acid esters and alkyl sulfate may be used in minor amounts. Alkyl hydroxamates have shown promise as cassiterite collectors at the laboratory scale.
Coal (covered elsewhere in the handbook)	Coal, pyrite, silica, clays, and carbonates	Low-ash, low-sulfur coal concentrate (selectivity against pyrite and other mineral impurities)	Flotation is typically conducted on fine coal (–0.5 mm) fraction from coarse coal cleaning stage. Primary collectors are petroleum hydrocarbons such as diesel fuel, heavy fuel oils, and kerosene, often as formulations with alcohol and glycol frothers.
Feldspar	Orthoclase, microcline and albite, with gangue minerals silica sand, muscovite, biotite, tourmaline, garnets, ilmenite, and other iron oxides	Separation of feldspar from gangue minerals	Sequential flotation of mica, iron oxides (and other heavy minerals), and feldspar. The flotation feed is attrition scrubbed at ~70% solids and is *deslimed.* Mica flotation: Conditioning deslimed feed at 50%–60% solids at a pH of 3.0–3.5 using sulfuric acid. The feed is diluted to ~20%–30% solids and mica is floated using a cationic collector such as tallow amine with fuel oil (if necessary). Iron oxides and heavy minerals flotation: Any residual mica is also removed in this stage. Mica flotation tailings are dewatered and conditioned at 70%–75% solids at pH 2.5–3.0. The pulp is then diluted to 20%–30% solids, and flotation is conducted using strong petroleum sulfonates. Feldspar flotation: Tailings from the second stage are dewatered and conditioned at 50%–60% solids at pH 2–2.5 using sulfuric acid. HF is added to activate feldspar and depress silica. Feldspars are then floated at 20%–30% solids using a primary long-chain alkyl amine such as tallow amine with kerosene or No. 2 fuel oil.
Fluorspar	Fluorite and gangue minerals quartz, barite, calcite, and other carbonates	Rejection of gangue minerals to produce high-grade fluorspar concentrates (>97% CaF_2 for acid-grade concentrates, >80% CaF_2 for metallurgical- or ceramic-grade concentrates)	Selectivity in fluorite flotation is paramount because of the stringent specifications of acid-grade concentrates (>97% CaF_2, <1.0% SiO_2, 1.5% $CaCO_3$, 0.5% Fe_2O_3). The typical reagent scheme includes Na or NH_4 carbonate as a pH modifier and clay slimes dispersant. Sodium silicate, quebracho, starch, or tannin is used to depress calcite, silicates, and other carbonate minerals. High solids (~45%–75%) and high temperature (55°–85°C) conditioning is often needed to achieve desired selectivity. Fluorspar flotation is achieved using oleic acid or very-high-grade tall oil fatty acid. Partial replacement of fatty acid with the more selective alkyl sulfosuccinamate may improve performance. Alkyl sulfosuccinamate may also be used in conjunction with modifiers as the sole fluorspar collector. In ores with high phosphate content, the use of functionalized polymers to depress phosphate impurities prior to collector addition can improve fluorite concentrate grade.
Iron ore	Hematite, magnetite; gangue minerals: quartz, other silicates, goethite, apatite	Direct flotation of iron oxides and reject gangue minerals (not common)	High solids (50%–65%) conditioning at pH 3–5 using sulfuric acid and petroleum sulfonates. Depending on the type of gangue minerals present, formulated fatty acid can be used. Difficult ores that cannot be treated with petroleum sulfonates and fatty acids can be floated with hydroxamate collectors.
		Reverse flotation of quartz and other silicates (most common)	For high-iron/low-silica-grade ores, reverse flotation of silica is practiced using ether amines or diamines. Iron oxides are selectively flocculated and depressed using causticized starch. Sodium silicate is used as a dispersant. Desliming is often necessary to reject fines and slimes which interfere in flotation.

(continues)

Table 18 Main industrial separations: Non-sulfide minerals (continued)

Ore	Main Value and Gangue Minerals	Desired Separation	Typical Reagent Scheme(s)
Kaolin clay	Kaolinite, with impurities iron oxides, anatase, silica, feldspar, mica, sulfides, and organic matter	Rejection of colored impurities and other gangue minerals	Low- to medium-grade kaolin clays are typically produced using dry processes such as air flotation, sizing, and magnetic separation. It is common to incorporate froth flotation depending on the desired grade. High-grade kaolin clays, on the other hand, are mostly produced by the reverse flotation of heavy and colored impurities such as anatase and iron oxides using hydroxamates and/or fatty acids. Sodium silicate, polyacrylate, and hexametaphosphate are used as depressants and dispersants. High solids (50%–70%) and high-intensity conditioning is typical during blunging and after collector addition. pH is ~7.5–9. Column flotation is common. Also, the combined use of other processes such as high-gradient magnetic separation and selective flocculation enables production of kaolin clays that meet strict specifications such as high purity and brightness. Fatty acids require $CaCl_2$ as an activator. Hydroxamic acids do not require activator and provide far better performance (yield and brightness), even with "hard to process" clays.
Mineral sands	Rutile, anatase, zircon, tourmaline are the main heavy mineral sands with gangue quartz, feldspar, clays	Separation of heavy mineral sands from quartz	Desliming and conditioning at high pulp densities (68%–75%) with TOFA. For ores too coarse for flotation, grinding with the addition of a small amount of fuel oil may be required. pH ~8.5 adjusted with soda ash. Flotation concentrate is typically ~80% heavy minerals and ~20% quartz. Tailings are high-grade quartz product. In ores where feldspar occurs with quartz and the Al_2O_3 content of the final quartz product needs to be reduced, a quartz-rich concentrate is floated off from the tailings using an amine and a feldspar depressant. Liberated feldspar is rejected along with clays and other gangue minerals.
Potash	Sylvite and carnallite are the main value minerals. Halite is the main gangue mineral.	Direct flotation of sylvite and carnallite from halite and removal or depression of water-insoluble slimes	Flotation of sylvite (KCl) from halite (NaCl) in saturated brine at high temperature (30°–50°C); some plants try to operate at lower temperatures. Changes in temperature impact the solubility, and hence the performance of the amine collectors. Primary short-chain amines are preferred for low-temperature operations while long-chain amines are more effective at high temperatures. Recovery of coarse sylvite is an important goal. Therefore, hydrocarbon oils are used as "extenders." Ores containing high content of insoluble slimes, usually clays and carbonates, are difficult to process since these minerals compete with sylvite for the amine collector. Fully neutralized long-chain amines are preferred for these ores. Slime-blinding reagents such as carboxymethylcellulose, dextrin, guar gum, or functionalized polymeric depressants are added during the conditioning stage.
		Reverse flotation of halite from sylvite or carnallite	The reverse flotation of halite from sylvite/carnallite is preferred in some ores such as those found in the Dead Sea region in Israel and Jordan. In this process, alkyl morpholine type collectors are used.

(continues)

Table 18 Main industrial separations: Non-sulfide minerals (continued)

Ore	Main Value and Gangue Minerals	Desired Separation	Typical Reagent Scheme(s)
Phosphate	Phosphate minerals (fluorapatie, hydroxyapatite, francolite, phosphorite, collophase, etc.). Common gangue minerals are quartz, carbonates, mica and clays, and clay-type minerals.	Selective separation of phosphate minerals of igneous origin from gangue minerals	Apatite ores (with ~7% P_2O_5 or greater) with low carbonate content are relatively easier to process by flotation than ores with high mica and calcite content. Desliming is necessary. Feed is typically conditioned with sodium carbonate pH ~10. Sodium silicate, causticized starch, and guar are typically used as depressants for silicates, carbonates, and iron minerals. Primary collectors are TOFA, petroleum sulfonates, and alkyl sulfosuccinamate (which improves selectivity and recovery of fine apatite). If the ores contain magnetic or weakly magnetic iron oxides, the rougher concentrate is upgraded using magnetic separation to produce a high-grade phosphate concentrate (at least 36% P_2O_5).
		Selective separation of sedimentary phosphate minerals from gangue minerals	The "double flotation" (Crago) process is widely used for sedimentary ores. In the first stage, after desliming, high solids (~70%–72%) conditioning with soda ash or NaOH, a fatty acid formulation, and fuel oil (extender oil) at pH ~9.0–9.5, phosphate minerals are floated from silicates and clays. Short conditioning and flotation times are used. In the second stage, the phosphate concentrate is scrubbed with H_2SO_4 to remove collector and fuel oil coating from the solids (de-oiling), followed by washing and dewatering to remove reagents. The washed concentrate is conditioned with a fatty amine and diesel fuel oil at slightly acidic to neutral pH to float silica. The use of polymeric phosphate depressants improves selectivity. Short conditioning and flotation times are used. Some high-grade phosphate ores with low silica content can be processed without the need for the "double flotation" method. A high-grade concentrate is typically produced by floating the silica gangue into the concentrate using amine collectors and polymeric phosphate depressants. Ores with high carbonate content (dolomite and calcite), reverse flotation of carbonates is achieved at low pH (~5–5.5 with sulfuric acid) using formulated fatty acid collectors. Phosphoric acid and sodium polyphosphates are used as phosphate depressants. High solids conditioning with short conditioning time and flotation time are typical.
Tungsten	Scheelite and wolframite are the main value minerals	Separation of tungsten minerals from gangue minerals such as calcite, sulfides, and phosphate minerals	Tungsten ores are generally amenable to gravity concentration because of the large specific gravity difference between tungsten and gangue minerals. However, most tungsten minerals are finely disseminated in gangue minerals, which necessitates fine grinding and at least one flotation stage to recover the fine tungsten minerals. Flotation is usually conducted in alkaline pH (adjusted with soda ash, caustic, or sodium silicate) using TOFA. The use of formulated TOFAs provides better metallurgical performance at lower dosages than straight TOFAs. Presence of calcite necessitates the use of depressants such as quebracho or tannic acids. If the main value mineral is wolframite, flotation is typically performed in an acid circuit where petroleum sulfonates are used in conjunction with fuel oil. Alkyl hydroxamic acids may provide improved recovery and selectivity based on lab-scale experiments. For ores containing sulfide minerals, a preliminary sulfide flotation stage using xanthate is employed prior to gravity concentration (tabling) and flotation of tungsten minerals.

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