

algae and humic substances. The first water treatment plant based on the DAF process was established in South Africa in 1969. Since then it has received worldwide attention for research and development on all aspects of DAF.

The first DAF plant in the USA was set up at the Millwood water treatment plant in Westchester county (35 miles north of New York city) in August 1993. Now, several other plants based on DAF are operating or are under study in the USA. It is postulated that DAF is an emerging technology in the USA that will become more important because of existing and proposed regulations that require filtration of surface waters and increased removal of protozoa cysts such as *Cryptosporidium* and *Giardia*. Large scale pilot-plant trials of water treatment have been carried out in the UK for removal of *Cryptosporidium* using DAF. Well-operated chemical coagulation-based treatment using DAF should be capable of achieving 99% removal of *Cryptosporidium* oocysts.

DAF is also used in the forest industry, food-stuff industry, meat-processing industry, seafood industry, potato processing, pulp and paper industry, petroleum industry, poultry industry, producing refined sugar from raw juices, separation of grease, oil, fibres and other low density solids, chemical processing plants, storm water cleaning, and other similar industries.

Future Trends

There is great potential for DAF. Its use has been limited due to lack of knowledge of the process by users, designers and other regulatory agencies. The

design and operation of DAF methods are currently tested on empirical data and data from costly and time-consuming pilot-plant models. More information is needed on the performance, designs and costs of the DAF process.

See also: I/Flotation.

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Electrochemistry: Contaminant Ions and Sulfide Mineral Interactions

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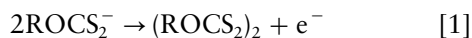
Introduction

Mineral separation by flotation is based on the selective levitation and separation of mineral particles by gas bubbles. This is carried out by the selective conversion of the surfaces of the minerals to be floated

from their typical hydrophilic nature to hydrophobic, to which the gas bubbles may attach to effect the levitation. This conversion is usually achieved by the selective attachment of collectors to the surface of the mineral or by natural processes; an example of the latter is the formation of elemental sulfur or a metal-deficient sulfide layer on sulfides.

Typical collector agents are organic substances consisting of an ionic, i.e. hydrophilic, end that attaches to the mineral and a nonionic hydrocarbon end that creates the hydrophobicity of the mineral surface. A widely used collector in selective sulfide flotation is the xanthate ion (O-alkyldithiocarbonate, ROCS₂).

Most of the sulfide minerals are electronic semiconductors or electrically conductive. This implies that the reactions required for the creation of a hydrophobic surface on sulfides may be electrochemical. For example, the xanthate ion may be oxidized at an anodic area of a local cell on the mineral surface to form hydrophobic dixanthogen:



The corresponding reduction reaction is the catalytic reduction of oxygen. Apart from this type of electrochemical reaction, electrochemical interaction between dissimilar sulfide minerals of different rest potentials occurs when there is electrical contact between them in a sufficiently conductive electrolyte, and this is of a galvanic nature. For contact of this nature to occur the various sulfides must be either present in composite particles, i.e. middlings, or be brought into such frequent collision contact in the flotation pulp, that significant electrical charge transfer can take place. In the laboratory these phenomena can be studied by electrically connected mineral electrodes, or stirred/fluidized beds made up of sulfide minerals only. Although these laboratory methods indicated significant electrochemical interaction, studies conducted at the authors' laboratories on simulated mineral feed of realistic plant composition showed no significant charge transfer. This was possibly due to the complexity of the flotation pulp chemistry, which makes it difficult to distinguish between the contribution of chemical and electrochemical processes to overall plant performance.

Theory and Principles of Electrochemical Interaction between Mineral Species

Reactions on mineral surfaces in which there is a change of oxidation state for the species involved are generally electrochemical in nature. This adds to the complexity of multi-mineral systems, in the sense that, apart from interactions through a common aqueous phase, by for instance dissolution-precipitation reactions, galvanic interactions through electrical contact between minerals must be considered also. Galvanic interactions between minerals will cause the more inert mineral to act predominantly as cathode, and reduction of dissolved oxygen would typically occur on its surface. This will stimulate anodic counter-reactions such as the oxidation of xanthate to dixanthogen or metal xanthates and that of metal sulfides to metal-deficient sulfides or elemental sulfur,

all of which will promote hydrophobicity on the surface of the more reactive mineral.

Similarly, contact of a less reactive sulfide mineral particle with more reactive steel, generated in abundance by industrial grinding operations, in the form of loose particles or layers smeared onto the mineral surfaces, may depress the mixed potential of the galvanic couple to such an extent that the oxidation reactions necessary for the hydrophobization of the sulfide surface will be slowed down. In extreme cases, reactions may become thermodynamically impossible.

In the following sections the role of electrochemical interactions in the separation of complex sulfide ores will be further explored. Particular attention will be paid to the use of pulp potential as a monitoring and control tool and the role of electrochemical reactions in the development of hydrophobicity.

Mixed Potential Theory

The interaction between collector reagent and mineral takes place at the mineral-solution interface. For ease of reference, and in view of the vast body of investigative work done on it, our discussion will focus on the use of xanthates as collector agents. In the case of sulfide minerals, which are generally semiconductors, the interactions with xanthate collectors involve charge transfer across the electrical double layer at the solid-liquid interfaces. Woods *et al.* suggested three ways by which the xanthate ion could confer hydrophobicity to a mineral surface. Firstly the anodic reaction leads to dixanthogen formation (see eqn [1]). Secondly they distinguish between dixanthogen produced by the anodic reaction of the xanthate ion and the xanthate ion adsorption at a lower potential which is held by electrostatic attraction:



Finally there is chemisorption for which the anodic oxidation of the xanthate ion on lead sulfide is:



The corresponding cathodic reaction typically requires the reduction of oxygen in industrial flotation systems. If it assumed that the process is Faradaic in nature, i.e. no charge accumulation can occur, the oxidation and reduction reactions will be coupled by the flow of charge. The rate of the electrochemical reactions can now be determined by considering the driving force available for the process and the kinetics of the individual processes. If the respective electrical

and ionic resistance of the mineral and solution is low, the system will with time reach a common potential called the 'mixed potential' at which the individual reactions will take place at steady state. This will typically be the case for solutions with a high salt loading and with anodic and cathodic areas in close proximity. The situation may be further complicated by the involvement of more than two half cell reactions and also by cathodic and anodic areas of varying sizes as is typically the case in galvanic interactions.

The mixed potential theory has been used to account for the collectorless flotation of sulfide minerals such as chalcocopyrite, by considering the contributions of both surface oxidation and oxygen reduction reactions to the common potential. For example, Trahar has shown that surface oxidation of sulfide minerals results in the formation of hydrophobic sulfur layers and thus enhances flotation. It has been suggested that for sulfide minerals, surface oxidation involves the progressive removal of metal atoms, leaving a hydrophobic, metal-deficient sulfide layer with a crystal lattice only marginally altered from the original structure. More recent studies by Buckley and Woods, using X-ray photoelectron spectroscopy, have confirmed that sulfur species are indeed formed on the mineral surfaces. The concepts are summarized in Figure 1.

In the presence of xanthate collector conditions for the formation of dixanthogen have been shown by Allison *et al.* to occur when the rest potential of the mineral is greater than the reversible potential of the xanthate/dixanthogen couple E_R (0.13V at pH 7.0), which for these minerals is the active collector species in xanthate-based flotation, except for galena, where the metal xanthate was indicated, as discussed by Cheng and Iwasaki (see Further Reading). The rest

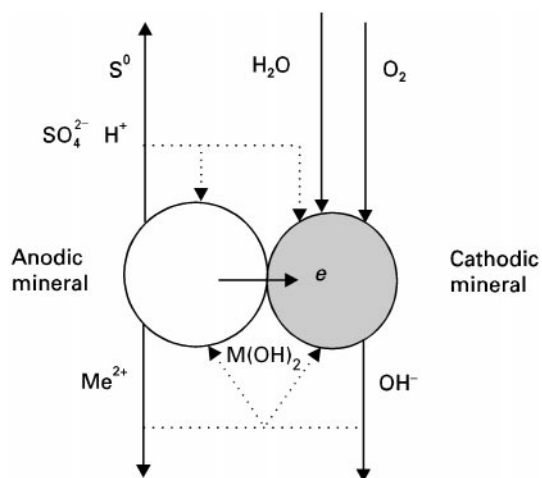


Figure 1 Generalized depiction of galvanic interaction between electrically connected particles.

Table 1 Rest potentials at various dissolved oxygen contents (Reproduced from Cheng and Iwasaki (1992) with permission Copyright Gordan and Breach Publishers.)

Mineral	Rest potential (V vs SHE) in $6.25 \times 10^{-4} M$ KEX solution	Range reported at 0–7 ppm O_2
Mild steel		– 0.515 to – 0.255
Sphalerite	– 0.15	
Stibnite	– 0.125	
Realgar	– 0.12	
Orpiment	– 0.10	
Antimonite	– 0.09	
Covellite	+ 0.05	
Bornite	+ 0.06	
Chalcocite	+ 0.06	
Chalcocopyrite	+ 0.14	0.115–0.355
Galena	+ 0.14	0.142–0.172
Molybdenite	+ 0.16	
Pyrrhotite	+ 0.21	0.055–0.290
Pyrite	+ 0.22	0.389–0.445
Arsenopyrite	+ 0.22	0.277–0.303

potential of a mineral surface, is the potential associated with a finite reaction rate in a specific solution environment (see Table 1). This is illustrated by Figure 2 from the work of Gardner and Woods, which

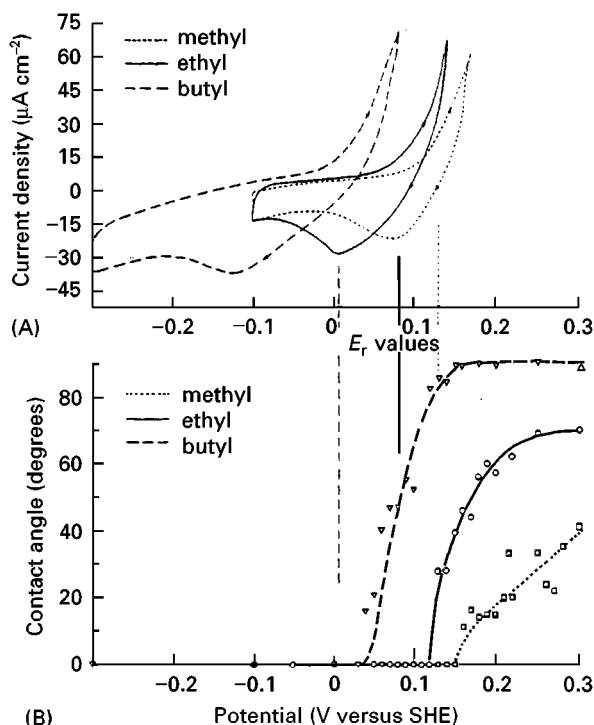


Figure 2 Pyrite electrode at 25°C in 0.05 M $Na_2B_4O_7$ solution (pH 9.2) containing 1000 ppm of three potassium alkylxanthates. (A) Cyclic voltammograms at $4 mV s^{-1}$; (B) Contact angles measured after holding the electrode at each potential for 30 s. The vertical lines are the E_r values for the xanthates. (Reproduced with permission from Gardner and Woods (1977) Copyright CSIRO Publishing.)

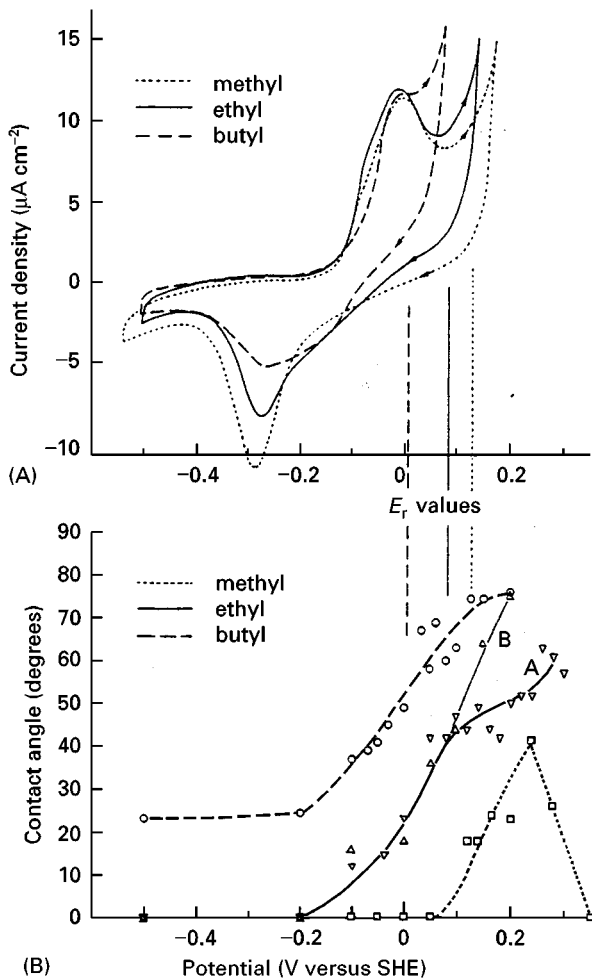


Figure 3 Galena electrode at 25°C in 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ solution (pH 9.2) containing 1000 ppm of three potassium alkylxanthates. (A) Cyclic voltammograms at 4 mV s^{-1} ; (B) contact angles measured after holding the electrode at each potential for 30 s. The vertical lines are the E_r values for the xanthates. (Reproduced with permission from Gardner and Woods (1977) Copyright CSIRO Publishing.)

clearly indicates that of pyrite hydrophobicity only develops at potentials more noble than the reversible potential for xanthate/dixanthogen reaction. For galena the response shown in Figure 3 is somewhat different, with a significant current flow occurring below E_R due to the contribution of the chemisorbed reaction. It is also interesting to observe a zero contact angle at -0.2 V .

Galvanic Interaction between Sulfide Minerals in a Pulp

As indicated earlier, galvanic interactions arise between two or more dissimilar minerals, and/or metals that are in electrical contact with each other and with an electrolyte. Electrochemical reactions at the min-

eral surfaces result in coupled current and ion flows. The cathodic reaction is generally the reduction of oxygen to hydroxide, while the oxidation reaction involves the oxidation of the sulfide mineral. The current flow depends on the surface area and conductivity of the mineral as well as the chemical composition of the electrolyte.

Minerals can only be separated by flotation if they are physically separate, i.e. liberated from each other. Short periods of galvanic contact between sulfide particles are unlikely to result in the development of the longer-term hydrophobicity that would be required for flotation. Polarization studies by Gardner and Woods on lead sulfides have indicated that the formation of hydrophobic substances, in this case lead xanthate, is reversible and thus unlikely to endure long enough for bubble contact to be established. In the context of the selective flotation of sulfides it would be the middlings, where the different sulfides would still be in physical contact, that would be the most influenced by galvanic interactions.

In the case of middlings it is possible that the floatability may even be better than that of pure minerals, due to the greater spatial separation and electric potential differentiation of the anodic and cathodic sites on such composite particles compared to single mineral particles. The possibility for spatial separation will increase with increasing conductivity of the solution and will be more important in solutions of high salinity.

As an indication of the galvanic interactions that may develop between different sulfides, a list of rest potential values has been reproduced in Table 1. The rest potential values mentioned were determined at near neutral pH values and will generally decrease with increasing pH. Because of this effect, many sulfides may be depressed by an increase in pulp pH, as their potentials move further away from the dixanthogen/xanthate equilibrium potential.

This disregards any chemical changes that may occur on the mineral surfaces due to a rise in alkalinity. High pH conditions typically develop at the cathodic sites, which favour the precipitation of metal hydroxides and would encroach on the anodic reaction site if the spatial separation of the sites is not large.

Consider the flotation of a middlings particle containing chalcopyrite and pyrite. In the absence of a xanthate collector, pyrite acts as a cathode of the local pyrite-chalcopyrite cell. Oxidation of the chalcopyrite surface is the predominant reaction balanced by the corresponding reduction reaction on the pyrite surface.

Buckley and Woods demonstrated that the collectorless floatability of chalcopyrite and pyrite

middlings particles increases with the amount of quartz added. This was attributed to the adsorption of hydrophilic iron hydroxides from the sulfide mineral surfaces on the quartz surface.

The uptake of xanthate ion strongly depends on the rest potential of the sulfide mineral. For sulfide minerals with rest potentials above +0.13V, xanthate ions are oxidized at the mineral surface to dixanthogen, which imparts hydrophobicity to the mineral surface. For bornite and chalcocite, whose rest potential was below that of the xanthate/dixanthogen reversible couple, metal xanthate was identified. For sphalerite and stibnite, the reaction products could not be positively identified. Rao, Moon and Leja also indicated that contact between various sulfides and iron will result in the depression of the potential to such an extent that the oxidation of xanthate to dixanthogen will no longer be possible. This is indicated in Figure 4.

During electrochemical interaction between sulfide species, ionic charge transfer takes place through the flotation liquor, while electronic charge transfer takes place through the solid interface; solid phase conductivity, as well as water conductivity is thus important. As an example, it is the experience on the Phalaborwa igneous complex that plant water conductivities range generally between 180 mS (fresh industrial

water) and extremes of *ca.* 500 ms, with a middle range of 200–300 mS.

For separate mineral particles, the solid phase charge transfer would rely on particle collision, in which the gangue particles have a shielding influence. This reduces the galvanic interactions to a point where electrochemical interactions between fully liberated minerals are unimportant in flotation plant practice, unless plant waters are highly conductive, and both pulp densities and sulfide mineral concentrations are high enough.

Reaction Products Affecting Flotation Performance

General

The reaction products of galvanic interaction may influence the flotation efficiency of composite minerals by direct depression or activation of minerals, or by affecting flotation froth characteristics. These reaction products, as will be shown, are not unique to galvanic processes, but their rate of formation may be enhanced by such interactions. The spatial separation of the anodic and cathodic reactions in galvanic interactions favours the kinetics in the sense that the reaction products formed at the

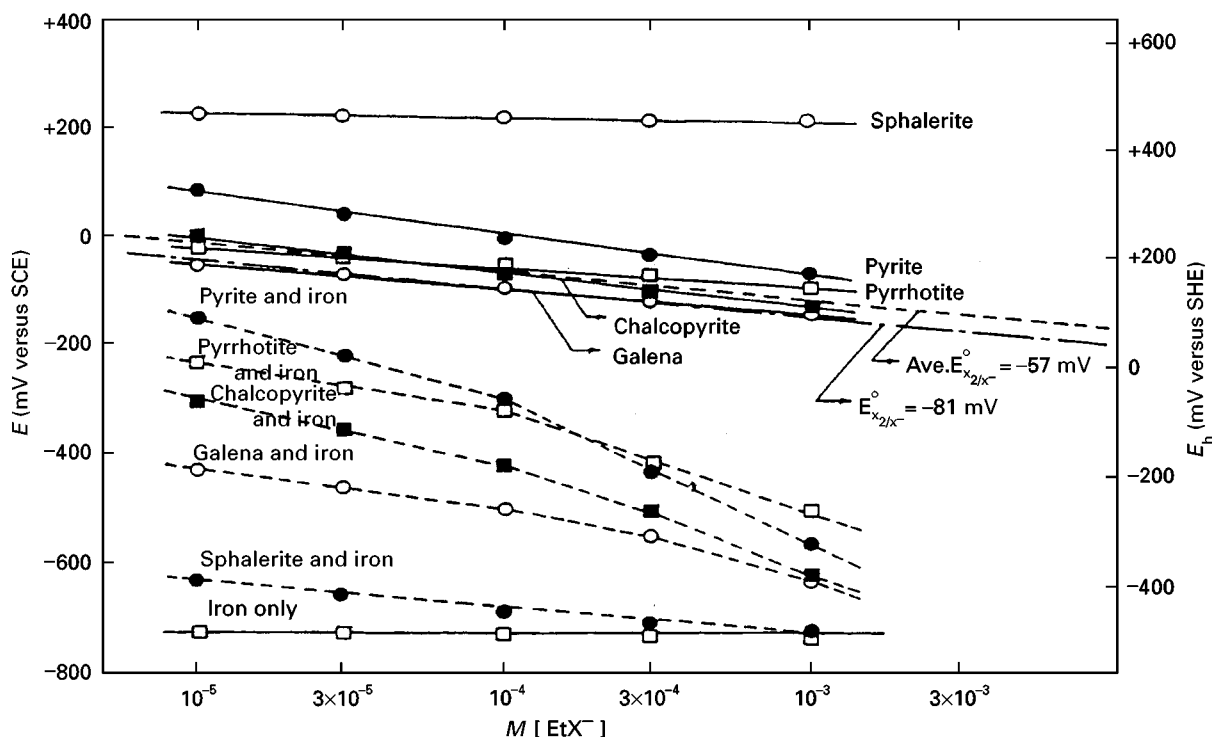
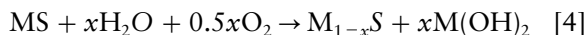


Figure 4 Mixed potentials of sulfide minerals alone and in contact with metallic iron as a function of xanthate concentration. Nonoxidizing conditions, argon purging – 400 cc min⁻¹ natural pH, 25°C. (Reproduced with permission from Rao, Moon and Leja (1976) *Flotation*, A.M. Gaudin Memorial Vol. Copyright American Institute of Mining Metallurgical and Petroleum Engineers.)

anodic and cathodic sites do not directly interact to deposit potentially reaction stifling product on the anodic site.

The reaction products of galvanic interaction between mineral species can be distinguished on the basis of their location. Firstly, the reaction product may take the form of a surface modification of the mineral, e.g. a metal-deficient sulfide layer, supported and to a greater or lesser degree stabilized, by the underlying, unaltered phase. Secondly, the product may be chemically distinct from, and physically attached to, the original mineral particle. Examples of this are elemental sulfur and ferrous hydroxide coatings. Finally, the reaction product may detach and remove itself from the original mineral, like sulfate anions, copper cations, or ferric hydroxide particulates.

The anodic reaction of sulfides is presently thought to lead to the formation of metal-deficient, sulfur-rich surface species, by releasing an active metal ion which may form a metal hydroxide ($M(OH)_2$):



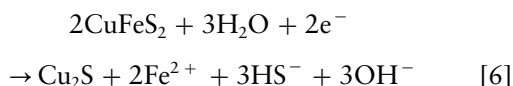
The formation of metal-deficient sulfide at the surface will tend to activate the surface and cause the metal hydroxy species to detach. However in the case of Fe^{2+} , species remain largely attached, leading to a blanketing effect that tends to hinder particle-bubble attachment. At suitable pH values, the release of reactive cations may lead to the unwanted activation of sulfide minerals, notoriously by copper ions.

As a general precaution against this reaction path, dissolved oxygen levels can be lowered. However, a lowering of pulp oxidative potential tends to lead to a general depression of flotation. An alternative is the elimination of metal-deficient sulfide species, or elemental sulfur, by reaction with aqueous sulfur dioxide:



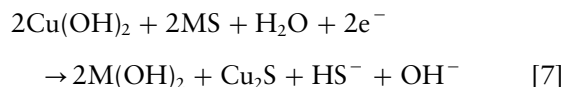
This is a possible mechanism for galena depression with sulfur dioxide in flotation, in addition to other mechanisms postulated, i.e. a lowering of copper ion activity in solution, xanthate decomposition and a lowering of the oxidative potential below that necessary for xanthate oxidation to dixanthogen.

A reaction path for the cathodic reaction of chalcopyrite, at neutral pH values and in oxygen-starved pulps, was also proposed by Li and Iwasaki:

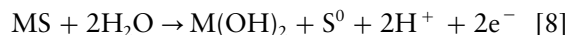


Activating Species

The release of activating species may be accelerated by galvanic interaction. Activation of sulfide species, raising their floatability above that which is achievable naturally, can occur due to an enhancement of the hydrophobicity of the mineral, or due to the insertion or attachment of ions which are more reactive towards collector reagents than the host species. In the latter case, the main, but not only, ion to consider is copper, which may attach itself to a particle as follows, by direct replacement:



The reaction path can be favoured by the presence of a suitable cathodic particulate mineral, like pyrite, reacting along the lines of the following equation:



The effect of galvanic coupling in a conducting particle will cause an electron flow, which will facilitate the simultaneous cathodic reduction of the MS surface by reaction with $Cu(OH)_2$, and the anodic oxidation of MS both reactions producing hydrophobic surface coverings of Cu_2S and S^0 , respectively.

Another example is the activation of pyrite by lead ions. In support of the assertion that true electrochemical interaction is limited to composite particles, Zhang *et al.* found, importantly, that interaction between composite particles containing pyrite and sphalerite was negligible in the absence of metal ions in solution. In their presence, sphalerite was found to successfully compete with pyrite for the activating ions, and through their action to compete more successfully for xanthate, thus depressing the floatability of pyrite. Competition for activating species thus seems to be an important factor in the interaction between minerals in flotation.

Depressing Species

The formation of hydrated, oxidized surface species like iron hydroxide and basic sulfates, increases particle hydrophilicity, and will thus depress flotation. High thiosulfate levels, which may arise when milling under relatively nonreducing conditions, e.g. fully autogenous grinding, or laboratory grinding in porcelain mills, may lead to the precipitation of insoluble thio-salts, which may also depress flotation. The generation of soluble sulfide species, especially notable in stagnant, anaerobic water reservoirs with bacterial action, may lead to mineral depression, since the

sulfide and xanthate ions compete for the same surface sites.

Froth Characteristics Affecting Species

The effect of froth structure on flotation is usually related to its stability. Stable froths have small bubbles and a high entrained water content. The solids in the entrained water are approximately at their concentrations in the pulp; consequently their overflowing concentrates will be of low grade. The presence or absence of fine, colloidal particles has a profound effect on flotation froth structure and drainage, and thus overall flotation performance. The most notable example of this is the deleterious effect that copious quantities of (naturally floatable) talc particles have on sulfide flotation, with adverse results in grade, recovery, and rates of recovery. The same froth modifying effects can be noticed when dealing with colloidal precipitates. In practice, the noticeable effects are largely limited to iron hydroxides, due to their abundance in natural systems. Thus, a change in froth structure may be noted when hydrated ferrous hydroxide particles are oxidized to (less hydrated) ferric oxide. The latter species allows a more desirable, less slimy, froth structure. As another example, it has been strongly suggested that the common practice of copper sulfate addition in flotation plants, apart from activating effects, also has strong froth structure modifying effects.

Application to Plant Practice

Collectorless Flotation

For collectorless flotation, the formation of a metal-deficient sulfide layer on the particle surface must generally be targeted. Formation of such a layer may be accelerated and spatially accentuated by galvanic interaction. When considering the flotation of sulfide minerals in the absence of collector reagents, in the context of electrochemical mineral interaction, three factors can induce floatability. First of all, floatability can be natural, i.e. due to the crystal structure and chemical bonding of a mineral. Examples of such minerals are molybdenite, stibnite, and the arsenic sulfides realgar and orpiment. Secondly, collectorless flotation can be self-induced, i.e. under the right pulp oxidative potentials, surface products will form which induce hydrophobicity. Examples of this are pyrrhotite and chalcopyrite. Rao and Finch found that pyrite/sphalerite selectivity could be enhanced by first recovering the pyrite which is naturally floatable, due to a chemically formed sulfur layer, in the absence of a collector. A third cause of floatability is mineral size. As minerals decrease in size, their

recovery into flotation froths increases due to entrainment, rather than selective attachment to froth bubbles. A good example of this is galena flotation from complex ores. At one mine site, carrying out sequential copper-lead-zinc flotation, about three-quarters of lead recovery into the copper concentrate was found to be made up of galena particles smaller than 10 μm . Since this effect is physical rather than chemical, it can only be significantly affected by a change in physical parameters, e.g. froth lamellae thickness and particle size.

In the collectorless flotation of pyrite-chalcopyrite-quartz mixtures, Johnson found a dependence of flotation behaviour on the pyrite/chalcopyrite surface area ratio, which would be consistent with electrochemical interaction. In this work it was however shown as well that copper solubilization was not enhanced in the presence of pyrite, but rather reduced; this points to copper deposition on pyrite – in other words, to activation rather than direct electrochemical interaction. Interestingly, interaction was reduced in the presence of quartz, due to adsorption of metal ions onto the quartz surfaces. In this respect, adsorption studies on other gangue minerals showed that such scavenging of potentially activating ions from solution may be substantial.

Pulp Oxidative Potential Control

Hayes and Ralston showed that the control of pulp oxidative potentials allows flotation selectivity, and is therefore a worthwhile approach in the flotation of complex sulfide ores, in addition to pH strategies. Direct electrochemical interactions between physically separated sulfide minerals, in which one affects the other's flotation behaviour directly through an anode-cathode relationship, have so far not been convincingly demonstrated on plant scale.

Galvanic and electrochemical interaction between sulfide minerals, and general chemical reactivity, is to a large degree dependent on the presence of oxygen in solution. The control of oxygen levels is thus generally the objective and result of pulp oxidative potential control. Since industrial flotation relies heavily on the use of ambient air, it has been proposed to regulate the oxygen concentrations entering flotation by admixture of nitrogen, or by partial re-circulation of process air released from the froth surface. The former approach is expensive whereas the latter depends on cells specifically designed to collect and re-circulate air leaving the top surface of the froth. Cylindrical cells seem to be most effective in this respect. The gas composition of bubbles generated by pressure differentials in flotation cells is dependent on a suite of factors, including the magnitude of

the pressure drop, dissolved substances, and nature of the nucleating surfaces. Benefits in flotation results were shown when regulating certain reagent additions on the basis of pulp oxidative potential, e.g. sulfuric acid, rather than pH. However, benefits might well be mostly due to froth structure improvements.

Trahar has shown that interactions between sulfide minerals were much decreased if they are ground separately, and only combined in the flotation cell. In this case, no mineral interaction between chalcopyrite, galena and sphalerite could be statistically proven. This demonstrates that galvanic interaction between sulfide minerals is only practically noticeable when mechanical contact exists. Grano *et al.* have also found that flotation selectivity between sulfide minerals is most sensitive to milling and preconditioning parameters, more so than to oxidative potentials during flotation itself, and mostly due to the presence of mild steel particles originating from equipment wear. For this reason, amongst others, research into comminution techniques which maximize mineral separation, whilst minimizing smearing, overgrinding, and steel consumption, must be a priority in the minerals industry. The effect of mild steel particles generated during ore comminution is mainly due to oxygen consumption, corrosion inhibitors being essentially ineffective. Full oxidation of these particles during conditioning removes their deleterious effect. Even for real ores containing significant quantities of more than one sulfide mineral, reasonable correlations exist between the behaviour of minerals in the ore and single minerals, as found by Grano *et al.* This indicates the limited extent of electrochemical mineral interactions in general practice.

Conclusion

True electrochemical interactions between sulfide minerals on industrial size plants are thought not to be of practical significance, except when physical contact between dissimilar sulfides exists (middlings), and/or at high pulp densities, high sulfide concentrations in the flotation feed, and high water conductivities. More importantly, sulfide minerals are found to interact through competitive adsorption of activating ions, the reduction of oxygen levels in the flotation pulp, and froth modifying activity of mineral oxidation products. Middlings particles, composed of two or more sulfides, do however experience electrochemical interaction, the result of which appears to be an enhancement of floatability, leading to a reduction in concentrate grades. The solution to such a problem is however more to be sought in comminution technology than electrochemical intercession.

Oxidative potential control offers advantages in industrial flotation separations, but its effect does not appear to be an interference with electrochemical mineral interactions.

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