# Challenges in Sulphide Mineral Processing

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**Abstract:** Scientists and technologists in world over are making large efforts to streamline the conventional technological schemes of ore processing, in particular froth flotation towards reducing overall costs, limiting the use of dangerous substances, decreasing waste streams and improving waste disposal. Hitherto, search for such innovations has been performed mainly empirically and there is an urgent need to shift these technologies to be more innovative and effective.

Understanding of the fundamental concepts of aquatic chemistry of minerals–selective adsorption and selective redox reactions at mineral–solution interfaces would impact innovating conventional flotation process. Molecular-level knowledge and coherent understanding of minerals contacted with aqueous solutions is required which underlie great opportunities in controlling mineral–solution interfaces towards the grand challenge of tomorrow's science and mineral processing technology.

Aqueous redox chemistry of sulphides and adsorption mechanisms, the problems of metal sulphides selectivity against pyrite and fine particle flotation have been highlighted and discussed in the light of literature. The requisite knowledge and research needs to address these issues have also been briefly presented.

## INTRODUCTION

Processes on minerals in aquatic media give the world as we know it. Understandings these processes is central to understanding the Earth and its sustainability and to developing technologies as diverse as ore processing, heterogeneous catalysis in solution, remediation of contaminants, radioactive waste storage and disposal, biochemical engineering, development of novel surfactants, sorbents, sensors, synthesis of novel materials and coatings, and especially in emerging nanotechnologies, where stringent control of materials and surfaces is crucial. Despite the obvious importance and the long history of chemistry of aquatic heterogeneous processes [1], many fundamental issues, especially related to sulphide mineral–water interfaces, are still unresolved or poorly understood.

The sulphide minerals are the most important, most diverse, and richest in terms of physical, chemical, and structural properties. Such diversity originates from the more complex crystal and electronic structures compared to other classes of materials [2]. The main reasons are found in the variety of oxidation states, coordination numbers, symmetry, crystal field stabilization, density, stoichiometry, and acid–base surface properties that metal sulphides exhibit. They truly are fascinating compounds, capable of insulating, semiconducting, showing metallic and magnetic behaviors with continuous or sudden transitions between these states. The combination of variety of properties and applications of sulphides makes redox reactions catalyzed by these minerals in aqueous solutions a very important subject of research from both fundamental and industrial standpoints. In this context, sulphides and oxides are phenomenologically interconnected since sulphides are usually covered by oxides – products of the sulphide oxidation.

Molecule-level knowledge of the mechanisms of the interfacial processes will certainly boost technological innovations in ore processing and remediation of organic and inorganic contaminants. For example, despite a more than one-century history of flotation – the major industrial process for mineral separation – suitable reagents and reagent regimes are still being developed mainly empirically and scientists are just in the beginning of understanding of basic principles of selective interactions of minerals with hydrophobizing reagents (collectors). One of the possible ways to selectively control adsorption of a collector is conducting redox reactions before or after its adsorption at the mineral surface, as used, e.g., in sulphide flotation with xanthates [3]. It is well known that the toxicity, solubility, sorption, bioavailability, and transport of elements in soil and aquatic systems are strongly dependent on the oxidation state [4]. At present, "natural" attenuation and amplification of target compounds in soils and waters as well as practical ways to control their concentration below the maximum contaminant level (MCL) are important environmental and economic issues [5-7].

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There are still persistent problems in sulphide flotation of metal sulphides selectivity against pyrite and among sulphide minerals, inadvertent activation of silicate gangue by metal ions, hetero-coagulation between sulphide and gangue minerals and recovery of fine particles. The solutions to the problems require new concepts and ideas, and an attempt has been made to highlight some of these issues in this paper.

## PROCESSING OF SULPHIDE MINERALS

### Aqueous Redox Chemistry of Sulphides

Quantifying and predicting redox chemistry of oxides and sulphides is separately motivated within geochemical, electrochemical, and technological communities. The geochemical importance of this problem is connected with the fact that oxides and sulphides, being key thermodynamic regulators and catalysts in natural waters, are central players in such fundamental processes as geocycling of elements, rock weathering and soil formation, and transport of aqueous metal species and contaminants. These minerals significantly impact bio-environment geochemistry of near surface systems by altering pH and redox conditions, thereby increasing or decreasing mineral bioavailability [8]. Charge transfer processes on semiconducting sulphide and compound oxide electrodes are today under intense investigation towards novel techniques for conversion of solar energy and environmentally clean fuels such as hydrogen [9]. Within a few years well over a thousand publications about this topic appeared [9]. Therefore, increased knowledge of electronic properties of the mineral surfaces, the detailed mechanisms of charge transfer across their interfaces, and driving forces in the interactions with species from solution will help in improving the research in this area of electrochemistry.

Despite significant steps have been taken theoretically and experimentally to obtain a molecular-level and coherent understanding of aquatic reactivity of sulphides [10-12], a general theory of redox chemistry of these solids in waters still does not exist. A significant property of solids is dependence of their reactivity in terms of the composition/concentration of the surface defects and these can be classified as monodefects and clustered (mesoscopic) defects. In heterogeneous gas-phase reactions on oxides and sulphides, monodefects are typically characterized by higher sticking coefficients for adsorbates and higher acidic/basic properties as compared to regular terrace surface sites [13-17]. The importance of the defect problem in geochemical and flotation community is now only becoming to be recognized [18]. The important role of clustered defects in the redox processes on iron sulphides has been revealed [19]. Mineral surfaces created by grinding are rich in mono- and clustered defects, and these surface defects can dramatically influence or even dominate aqueous reactivity of solids through control of speciation of adsorbed species. In addition, they can trigger electrochemical mechanisms of the redox process. However, there still is not much direct experimental evidence for higher reactivity of surface defect sites of metal sulphides, not to mention comparison of reactivity of the different defect sites [18].

For redox modification of mineral surfaces as a tool for providing adsorption selectivity, it is essential to investigate and answer the following questions: Do the mineral surfaces have intrinsic oxidizing and reducing sites? What are adsorp-

tion forms of the redox-active anions ubiquitous in geochemical systems (sulfite/sulphate, selenate/selenite, arsenate/arsenite, chromate, etc.)? How does introduction of $S^{2-}$, $CN^-$, $O_2$, and $H_2O_2$ before/after the anion adsorption influence this picture? How does the partitioning between adsorbed and adsorbed-and-reacted anions change with time? What are adsorption forms of redox-active surfactants (xanthates and dithiophosphates) in the absence and presence of the pre-adsorbed anions? How this picture is influenced by solvated $S^{2-}$, $CN^-$, $O_2$, and $H_2O_2$? What is the difference between the anodic semireaction paths on semi-conducting sulphides in the redox process controlled "chemically" and electrochemically with a potentiostat? It would be possible to develop a predictive general model of redox catalytic activity of wide band-gap metal sulphides from the above studies of redox reactions and specify the mechanisms of the reactions (chemical and/or electrochemical), and to correlate the data with the electronic structure of the interfaces and systemize the results.

### Mechanisms of Interfacial Processes

In the case of oxides, the chemical mechanism is commonly considered [4, 10, 11, 18], which implies one of the following charge transfer reactions: 1) from the solid to the adsorbate, 2) between sorbates, or 3) from the adsorbate to the solid. The main idea behind this mechanism is that catalytic effect of the surface is caused by a decrease in the energy needed to modify the solvent structure, the standard redox potential of the reductant, and steric hindrance of the oxidant-reductant interaction [20]. However, the chemical model does not explain different modes and different rates of the oxidation film growth on different minerals [21-23] as well as heterogeneous processes on sulphides [19]. A general disadvantage of this model is in its explanatory character, low ability to predict.

An alternative is the *electrochemical* mechanism, in which the anodic and cathodic semi-reactions of the sum redox reaction are spatially separated. This mechanism has been invoked for interpreting aquatic chemistry of semiconducting sulphides [19, 24-26] and photochemical reactions on both oxides and sulphides [9, 18]. Apart from the energy level redistribution among species in the (inner and outer) Helmholtz layer, this model takes into account semiconducting properties of the solid [27]. Provided the position of the Fermi level relative to edges of the conduction and valence bands as well as specification, relative density and position of the surface states are known, the electron-accepting and electron-donating abilities of different solids can be compared and correlated with the direction and rates of a particular heterogeneous redox reaction of sulphides. Manipulating redox potential at the surface has already been employed for controlling the adsorption form of xanthates in sulphide flotation [3]. However, wider applicability of such an approach has not been explored.

On heterogeneous surfaces a *pseudo-electrochemical* (PE) mechanism, to reflect that the electrochemical mechanism is activated at the edge of the surface heterogeneity domain, is expected. One of the reaction pathways [28] can be through adsorption of oxidizing species at the electron-donating surface sites and removing the localized (trapped) electrons. This allows holes to approach the surface at these

sites and oxidize adsorbed reducing species in the site vicinity. Another pathway consists of donating electron density from the sites with adsorbed oxygen to the neighboring sites with the adsorbed reductant, encouraging the transfer of an electron from the reductant to this oxygen in a manner analogous to the effect of hydrolysis on increasing metal ion oxygenation rates [29, 30]. In both the cases, the one counterpart of the redox reaction, being activated at the edge of the domain once formed, proceeds through enlarging the initial spot, not starting new ones. The suggested mechanism is consistent with developing of discrete oxidation patches on semiconducting sulphides [31]. Obviously, relative contribution of the different pathways depends on the electronic properties of the mineral bulk and surface. It is important to study this regularity, the PE mechanism, and its specific pathways. Furthermore, assuming that bacteria recognize favourable materials for colonization through redox sensing [32, 33], one can suggest that there can exist a "redox" source of enhanced and selective reactivity of minerals with redox-active solutes: Oxidation/reduction of the mineral surface before or after adsorption of a redox-active solute can cause its selective immobilization.

## Flotation Selectivity Between Pyrite and Non-Ferrous Sulphides

Suitable reagents and reagent regimes are still being developed in flotation mainly empirically and scientists are just in the beginning of understanding of basic principles of selective interactions of minerals with hydrophobizing reagents (collectors). Given the economic concerns that bad selectivity for non-ferrous sulfide minerals against pyrite presents, there has been an intense scientific and technological effort to understand floatability of pyrite in the complex sulfide flotation and to develop methods to selectively protect the pyrite surface from the deleterious effects of the formation of sulphur-rich/elementary sulphur coatings and/or the collector adsorption [34, 35].

The use of $NaHSO_3$ as a flotation depressant [36, 37] is being practiced in selective flotation of sulphide minerals. The depressing effect generally increases from copper sulphides to galena, pyrite and sphalerite [38]. However, there is no common agreement about the depression mechanisms. In particular, the following three effects have previously been proposed for depression of pyrite flotation by $SO_3^{2-}$: 1) stripping/decomposition of xanthate [39]; 2) reaction with the pyrite surface to form hydrophilic iron oxides [40]; and 3) a decrease of redox potential of the pulp below a level at which binding/oxidation of a collector (electron donor) becomes energetically unfavorable [41]. In the presence of copper, sulphite was shown [42] to promote the oxidation of copper on the pyrite surface, preventing the adsorption of xanthate and thus leading to the mineral depression, but has no effect on sphalerite. At the same time, in the case of chalcopyrite, it was postulated [43, 44] that sulphite removes the adsorbed iron oxyhydroxide phase from the surface, leaving a sulfur-rich sulphide layer, which in turn promotes collector adsorption. Also, it was found [45] that the depressing effect of sulphite on chalcopyrite flotation depends on the presence of $Fe^{3+}$ ions released from grinding media. Apart from the decomposition of xanthate/dixanthogen and the decrease in xanthate adsorption following a decrease of the redox potential of the pulp, several additional mechanisms have been put forward to explain the depression of the flotation of sphalerite [46]. They include: the formation of a zinc sulphite hydrophilic layer at the mineral surface; the reduction of copper-activation as a result of consumption of copper in solution as copper sulphite; and the consumption of dissolved oxygen. Sulphite ions are also known to react with polysulphide or elemental sulphur and form thiosulphate ions [47]; a decrease in surface hydrophobicity is therefore expected from this reaction. Finally, compared to sulphate, this reduced sulfoxyanion has higher adsorption affinity due to lower S–O bond order [48]. Therefore, we can expect that sulphate anions produced upon catalytic oxidation of sulphite species will much more strongly be bound to the sulphide surface compared with the sulphate anions that are directly adsorbed through ion exchange/outer-sphere complexation, thus competing more efficiently with collectors for the adsorption sites on sulphides, which may strengthen the depressing effect of sulphite. This effect, if properly understood, can open a new cost-effective approach to selectively regulate surface properties of sulphides.

Recently, it was revealed [49, 50] that ferric defects on ground pyrite surfaces can generate $OH^{\bullet}$ radicals upon interaction with water. It may be the existence and reactivity of $OH^{\bullet}$ that plays a crucial role in catalytic degradation of organic pollutants by pyrite [49]. However, participation of these species, if any, in non-selective oxidation of the pulp components and hence in deteriorating the concentrate grade has not still been explored yet. To fill the gap, it is important to build correlation between percentage of pyrite in the concentrate, grinding conditions and concentration of $OH^{\bullet}/H_2O_2$ in the pulp as well as to study possible ways of flexibly controlling the formation of these species through known chemical means for depressing the generation of the oxidant. One of such ways can be addition of chloride ions, which are known to inhibit the deposition of elemental sulphur on the pyrite electrode surface by promoting the oxidation of an adsorbed intermediate, believed to be the thiosulphate ion, to soluble tetrathionate ions. In the absence of chloride ions, the thiosulphate intermediate undergoes acid decomposition on the pyrite surface to yield elemental sulphur [51].

For the problem of low selectivity against pyrite, the effect of production of $H_2O_2$ by pyrite on degradation of flotation selectivity needs to be examined. To pinpoint the dominant contribution (natural hydrophobicity, formation of elemental sulphur on the surface under the flotation conditions, and/or activation) to low selectivity of sulphide flotation against pyrite, the surfaces of pyrite particles from both concentrate and tailings need spectroscopy characterization for surface speciation.

## Fine Particle Flotation

The other critical problem relating to bad selectivity of flotation is the differences in floatability of fine and coarse particles. In particular, fine particles and colloids (slimes) of iron oxides and hydroxides are ubiquitous in mixed sulphide mineral flotation pulps, originating from the steel grinding media, iron sulphide minerals and non-sulphide gangue, degrade the quality of the concentrate [52]. Slimes have a significant depressant action on both the collector-induced and collectorless flotation of polysulphide ores [53]. Their deteriorating effect is three-fold: First, fines of non-sulfide

gangue report to concentrate. Second, valuable sulfides are lost due to low floatability of the fine particles and the third effect may be envisaged as non-sulphide gangue slimes covering the originally-hydrophobic sulphide particles through heterocoagulation mechanism, rendering the particles hydrophilic. The low rate of flotation of fine particles is a result of a slow kinetics and the so-called 'high surface area' effects [54]. The former is due to low momentum through the pulp resulting by the small mass of fines and leads to lower probability of collision with passing air bubbles. In the not too distant past, the 'high surface area' effects have been assigned to a more rapid and inhomogeneous consumption of reagents, due to a higher relative proportion of the catalytically active crystallographic facets and surface defects (kinks, edges, corners, vacancies) in the exposed surface as well as to increased rates of solubility for particles [54, 55].

Attempts to remove and discard slimes before the enrichment operation result in significant economic losses to mineral processing companies [56, 57]. On the other hand, the continual reduction in grade is forcing miners to produce ultrafine particles in order to liberate mineral particles from the ore [58]. Although the problem of fines/nanoparticles (NP) in flotation is partly connected with the low mass and high surface area, other factors, such as surface composition, oxidation, mineralogical alterations, and dissolved ions concentration, etc., can play the decisive role in the phenomenon [59]. It is now widely agreed [60] that advances in ultrafine flotation technology through modifying well-established surface-based methods are better than developing entirely new processes.

However, recent data on structures of submicron and nanoparticles (NP) [61, 62] imply that the above picture is incomplete, while other factors, such as stoichiometry and the lattice structure can play the decisive role in the phenomenon. There is a common agreement that inherent reactivity of nanoparticles differs when compared to the micron sized counterparts. In general, chemical reactivity of particles with size below 200 nm is characterized by existence of the *optimum particle size* [63, 64]. This effect is usually attributed to contribution of different opposing effects such as larger surface area and kinetic advantages [65], the relative proportion of the catalytically active crystallographic facets in the exposed surface [66], the surface concentration of edges/corners inactive in multi-site reactions [67] and bidentate complexes of ligands [68, 69], the rate of electron–hole recombination at the surface or in the bulk of the particle [63], and changes in the structural and electronic properties of the particle due to quantum size effects [64].

It was shown [70] intrinsic difference in the surface and bulk stoichiometry and crystal structure of nano-particles from those of the corresponding large bulk crystals, also contribute to the optimum particle size effect. There are at least three effects that can contribute to the surface versus bulk difference in stoichiometry. First, the surface structure is not just a truncated bulk: It is stabilized by a significant surface relaxation and reconstruction [71-73]. Atoms exposed on the surface of a nanocrystal experience an anisotropic environment. To lower free energy per unit surface, the crystal structure of the near surface region is distorted, which under real conditions is accompanied by adsorption of water/hydroxyls.

In particular, it was recently established for iron oxides [74-78], in particular hematite [74] common with isostructural corundum, experiences either the "alfa to gamma" or "alfa to ferrihydrite" phase transitions at particle size below a certain threshold depending on the synthesis method and environment. This allows us to suggest that a decrease in particle size not only increases spacing between adsorption sites, as reported earlier for goethite [61], but also regularly changes their environments, affecting acid-base and redox properties of the mineral, coordination and speciation of adsorbed species and hence chemical activity of the mineral, in particular with flotation collectors. The lattice structure of sphalerite is NP size sensitive, changing from the zinc blende (cubic) to wurtzite (hexagonal) type with decreasing NP size. In the specific case of flotation systems, the grinding operation can additionally alter chemical properties of particles through mechanoactivation, galvanic interactions, and adsorption of cations and anions, which is also believed to be size dependent. Thus, to shed light on solution and solid state chemistry of submicron particles and to get a possibility to control their reactivity, which is important for many technological applications, including first of all flotation, it is necessary to perform a systematic study of how and why reactivity of sulphides changes with particle size.

Based on the above discussion, it is expected that with decreasing particle size the redox potential of the sulphide decreases, along with sorption capacity per $nm^2$. These effects can be balanced by using the more easily oxidizable homologues of xanthate and carbamate with longer chain lengths and/or employing sterically appropriate chelating legands with flexible distance between the reactive groups. The particle size effect needs to be addressed from a perspective not only to overcome the detrimental effect of sulphide fines but to employ the size-induced alternations in the surface and interior structure of the particles as a novel source of enhanced and selective reactivity of sulphides. Additionally, the presence of nanopores and molecularly confined spaces affects the reactant transport and hence the chemical reactivity. However, the effects of nanoporosity as well as nanosize and particularly the relationship between the two and the sum result are currently poorly understood. Such fundamental additions to the aqua chemistry of minerals is an imperative to designing new flotation reagents or reagent schemes that employ the difference in the chemical activity of NPs to improve the flotation grade.

## SUMMARY

The molecule-level understanding of the aquatic solids interfaces is the key to innovate many society-formative technologies including ore processing, waste recycling and the environment protection that are based on stringent control of interfacial processes. Hitherto, search for such innovations has been performed mainly empirically in view of the phenomenological/ macroscopic character and low predictive capacity of available knowledge of minerals aquatic chemistry, especially when it treats heterogeneous redox processes and the absence of general concepts of selective interactions of minerals with solutes. This implies that fundamental additions to aquatic chemistry of minerals are one of the major demands of the day.

The understanding of mineral behavior in water has been developed during the past century based on wet chemistry observations and application of equilibrium thermodynamics, and, since mid-twentieth century, through adopting some concepts of colloidal, surface chemistry, and electrochemistry. More recently, surface physics has been introduced into this field. However, this discipline is still generally poorly involved in research. In fact, what we directly know about mineral surfaces is mainly based on the spectroscopic and microscopic data obtained on model clean ideal single-crystal surfaces, under high ultra high vacuum (UHV) and X-ray irradiation conditions. At the same time, it is well-known that removal of a solid from water can fundamentally change its surface chemistry, while X-ray beams can photoreduce the sample. Moreover, real mineral surfaces are substantially defective, especially those created in flotation by grinding, which can dramatically influence or even dominate the mineral reactivity. Another rather rough but commonly accepted approximation is in treating a mineral surface as two-dimensional (2D) world, i.e., as a static set of adsorption sites that do not interact with the mineral bulk and do not change upon adsorption, which is a rather primitive approximation. To further understand mineral surface one should consider it in close electronic and material interconnection with the two neighboring phases.

Thus, there are crucial gaps between surface science of the idealistic surfaces, the indirect, equilibrium and 2D character of the present basic concepts, and the needs to know what is exactly happening at the real mineral-solution interfaces at the molecular level and in real time. It is important to fill these gaps by placing emphasis on *in situ* spectroscopic methods of research, accounting for electronic structure of the interface and the solid bulk, reaction kinetics/transitory states, as well as for effects of surface defects. These tasks will be highly rewarded: Even small technological improvements would provide high economical and ecological return on investments, with regard to the tonnages of material treated and the multi-dimensional impact of ore processing, recycling and the environment protection technologies.

## ACKNOWLEDGEMENT

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