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LEAD AND ZINC ORES: FLOTATION

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Outline of the Problem

Today, owing to the limitation of sources and supplies of mineral raw materials and the need to treat ores of increasingly lower grades, as well as those which are fine, complex mineralogically, and refractory, new flotation technology must be developed.

Flotation is in fact the most common process in metallic mineral separation and is the main way for recovering such valuable metals as lead (Pb) and zinc (Zn), or copper (Cu) from ores.

It is known that separation by flotation of useful minerals from gangue in an aqueous pulp happens when particles with polar, hydrophilic or wettable surfaces remain in the liquid phase, whilst particles with apolar hydrophobic or not wettable surfaces adhere to air bubbles. Collectors or depressing/activating reagents modify surface characteristics of minerals thus influencing affinity towards water. Thus, research into new separation technologies is mainly concerned with the search for new flotation reagents.

In fact the value of a flotation concentrate containing a given mineral, from which a desired metal is extracted by a metallurgical process, decreases with an increase in the presence of minerals containing metals other than the one of prime interest. It is thus necessary to design new specific collectors to separate the desired mineral from the gangue. Collectors generally employed in flotation are surfactants that form, for instance, electrostatic bonds with the solids (Leja 1982). Difficulty therefore arises when a particular metallic mineral, such as Pb or Zn mineral, has to be separated from an ore of complex composition or low grade (complex sulfide ores) or when the surface properties of the mineral (oxidized Pb and Zn ores) make the response to flotation extremely poor. To overcome this basic drawback in metal ore flotation, the possibility of using new compounds endowed with a strong affinity for metals themselves has been investigated. The search for new reagents for mineral flotation therefore aims to discover collectors (or depressants) capable of linking more selectively with a given element present in the ore.

The present work deals with the recovery of Pb and Zn by flotation and reviews the main problems faced by research engineers in this field.

Complex Pb-Zn Sulfide Ores

Complex sulfide ores have been defined as those ores for which it is difficult to recover one or more selective product of acceptable quality and economic value with minimal losses and at reasonable costs. Complex sulfide ores are fine-grained, intimate associations of chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS), disseminated in dominant pyrite, and containing valuable amounts of minor elements.

Generally, collectors employed for sulfide recovery are of the thiol type, and the most commonly used are xanthates. A great number of studies have been carried out on xanthates, examining their adsorption mechanism by spectroscopic techniques such as infrared spectroscopy (Giesekke 1983, Kongolo *et al.* 1984, Little *et al.* 1961, Marabini *et al.* 1983), IR-ATR techniques (Mielczarski *et al.* 1987, Mielczarski *et al.* 1981), X-ray photoelectron spectroscopy (XPS) (Laajalehto *et al.* 1988, Page *et al.* 1989), and also by calorimetric techniques (Partyka *et al.* 1987, Arnaud *et al.* 1989).

However xanthates are active towards the whole class of sulfide minerals, rather than towards one individual mineral. Thus, in order to float a given mineral from a mixture of minerals belonging to the same sulfide class, modifiers are used in order to render the action of the collector more specific, and to improve separation efficiency (Finkelstein *et al.*, 1976).

However, there are many problems in this procedure and the desired results are not always obtained, especially in the case of minerals of a complex composition as in the case treated.

Hence the importance of seeking out collectors capable of linking selectively with one single given mineral rather than with the whole class. Selective linkage is possible if the collector structure incorporates active groups having specific affinity for certain cation characteristic of the mineral surface.

Thus, the search for new, more selective reagents for sulfide mineral flotation is mainly concerned with chelate-forming reagents. In fact, chelating reagents are particular complexing reagents consisting of large organic molecules capable of linking to the metal ion via two or more functional groups, with the formation of one or more rings, thus forming a very stable bond. The stability of metal chelates is influenced by many factors which govern the selectivity and specificity of the chelation reaction.

Examples of the use of chelating reagents in flotation were known from studies on traditional thiol collectors. In fact, both dixanthogen and thionocarbamate act as chelating reagents (Ackerman *et al.*, 1987).

There are many studies on chelating agents as collectors more selective than xanthates (Marabini *et al.*, Rinelli *et al.*, Usoni *et al.*, Barbaro *et al.*, Somasundaran) and a review on this topic has been published by Pradip (Pradip 1988). Use of reagents of chelate type offers the possibility of improving selectivity in the flotation separation of complex sulfide minerals (Marbini *et al.* 1990 and 1991).

Oxidized Zn and Pb Minerals

It is well known that there is a difference between sulfurized and oxidized minerals as regards their separation by flotation. It is easy to recover Zn from sphalerite and Pb from galena even using xanthate collectors but it is not the same for Zn from smithsonite ($Zn\ CO_3$) and Pb from cerussite ($PbCO_3$).

Flotation of Zn and Pb oxidized minerals is difficult because there are no known direct-acting collectors capable of producing single metal concentrates. The need for new specific collectors is felt particularly in the case of oxidized lead and zinc minerals because their surface – unlike that of the sulfide variety – is not easily rendered hydrophobic by the collectors generally used, to achieve efficient flotation. Furthermore, the solubility of these oxide minerals is high. Consequently the collector also interacts with metal cations which have gone into solution, thus greatly increasing the amount of reagent required for flotation. It is therefore common practice to sulfurize such minerals prior to flotation so as to prepare their surface to receive xanthates, the collectors generally adopted for concentrating sulfides. Generally the collectors normally used in beneficiation plants act only if the ore has been subjected to a preliminary sulfidization phase which is extremely delicate and critical. In fact, sulfurization calls for careful dosage to avoid rendering the mineral surface inert.

Thus classical collectors have an affinity towards given mineralogical classes, whilst chelating reagents – when chemically adsorbed on the mineral surface – have specificity towards given cations, independently from the mineralogical form of the solid.

However this approach also has two main disadvantages, firstly, excessive consumption (Marabini 1973, Marabini *et al.* 1983), and secondly, lack of an aliphatic chain which renders the mineral surface hydrophobic.

In fact the chelating reagents commercially available are almost all aromatic molecules without a long hydrocarbon chain; thus, although the chelated min-

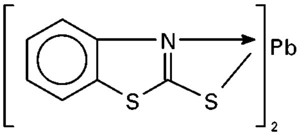

Figure 1 Structure of MBT-Pb chelate.

eral particle is fairly hydrophobic, it is not sufficiently aerophilic to ensure flotation. Studies on oxidized minerals (Usoni *et al.* 1971, Rinelli *et al.* 1973, Marabini 1975, Rinelli *et al.* 1976) were performed rendering particles hydrophobic by making contemporary available long-chain organic groups (as fuel-oil or oily frother) and chelating agents.

The first application of this concept is from 1973. A chelating reagent, namely 8-hydroxyquinoline (**Figure 1**) with fuel oil was used to float mixed oxide-sulfide minerals of Zn and Pb (Rinelli *et al.* 1973). Good recoveries have been attained on an ore containing 7.3% Zn with 1.4% as sphalerite, and 0.9% Pb with 1.4% as galena.

On the basis of the points made so far it is apparent that known chelating compounds form a class of reagents which can be used for the flotation of metallic ores, providing artificially the long chain organic portion by introducing a neutral oil (fuel oil). But the introduction of a new liquid phase into flotation pulp is damaging to the system as a whole and is not available on an industrial scale.

Studies, therefore, have been oriented towards the synthesis of new organic molecules containing both selective functional aromatic chelating groups and hydrophobic long alkyl chain portions. This is done by modifying known chelating collectors.

Indeed, much research was performed on the design of selective chelating collectors; this resulted in numerous structures being proposed and synthesized for laboratory-scale testing on lead/zinc ores prior to the performance of pilot-scale and plant-scale trials.

On the basis of a thermodynamic calculations for the selection of complexing collectors theoretically selective towards a cation (Marabini *et al.* 1983), two classes of reagents have been proposed by Marabini *et al.* (Marabini *et al.* 1988 and 1989, Nowak *et al.* 1991) for the flotation of oxidized Zn and Pb in a pilot plant. Much has been written on the role of the aliphatic chain in conventional collectors (Cases 1968, Predali 1968, Somasundaran 1964) but the work concerns new chelate-type reagents, of the mercaptobenzothiazole (MBT) and aminothiophenol (ATP) types having a mixed aromatic–aliphatic structure. The aromatic part contains specific functional chelating groups that are selective towards the zinc or the lead of oxidized minerals (MBT is selective towards lead and ATP towards zinc) while the aliphatic part consists of a hydrocarbon chain which renders the surface-complex hydrophobic.

The collecting action of MBT is thus attributable to the formation of a surface film selectively chemisorbed on the mineral surface rendered hydrophobic by the aliphatic chain.

In fact in the case of hydrophilic oxidized minerals, the aromatic-heterocyclic portion of the MBT alone does not suffice to render the surface sufficiently hydrophobic to ensure flotation. Hence an aliphatic chain has to be introduced in the molecular structure. The aliphatic chain is necessary to ensure a hydrophobic condition and hence collecting power for the aromatic chelating (MBT or ATP) reagent.

It has been demonstrated that three carbon atoms is the minimum chain length needed to ensure collecting power that improves with aliphatic chain length. Performance is enhanced slightly by the presence of an ether oxygen atom.

Where reagents of the ATP type are concerned, these (as the Schiff bases derived therefrom) exert chelating action towards Zn (Barbaro *et al.* 1997). Chelation occurs through weak bonds with nitrogen and –SH as shown (**Figure 2**).

The formation of a chemisorbed surface film is sufficiently stable to account for the collecting action. The selectivity of molecules containing ATP and different aliphatic chains has been studied by flotation tests.

In this case the role of the aliphatic chain and of the ether oxygen is of more decisive importance than for MBT in assuring the stability of the adsorbed phase and thus floatability. The selectivity increases with the number of carbon atoms in the chain.

In particular, the presence of the oxygen in the chain enhances selectivity, whilst in MBT class reagents only chain length is effective. This difference can be explained by the different chemical structure of the two reagents. In the case of MBT, the effect of the aliphatic substituent is due mainly to its hydrophobicizing effect, and thus to its

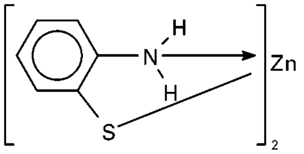

Figure 2 Structure of ATP-Zn chelate.

length which favours reciprocal attraction of the chains of the adsorbed layer.

By contrast, in the case of ATP, the effect of the aliphatic substituent is due not only to its hydrophobicizing effect, but also to its effect on reactivity of the aromatic polar head of the molecule. In fact the ATP chelating functional group has a weaker reactivity in comparison with MBT, and therefore is more sensitive to the effect of the substituent on its unique benzenic ring (whilst MBT has two aromatic structures). For this reason, in the case of ATP it is possible to observe that the presence of the oxygen in the chain greatly enhances selectivity. The positive effect of the R-O group in the para position *vis-à-vis* the nitrogen of ATP can be explained with the electron-releasing effect due to resonance of the oxygen with the benzene ring, which increases reactivity with the nitrogen group (Morrison 1973).

In the case of ATP, which forms a less stable bond with the mineral cation and which consists of a single benzene ring, the conjugative effect of the ether oxygen and the hyperconjugative effect of the alkyl groups are more evident than for MBT. Selectivity is improved by the insertion of oxygen in the chain and also by an increase in chain length. Here the effect of the alkyl chain on the aromatic functional group is more marked, permitting modulation of selectivity.

This research based on the design and synthesis of new flotation reagents opens new possibilities in the field of metallic Pb and Zn mineral recovery by flotation.

See also: **II/Flotation:** Hydrophobic Surface State Flotation.

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