ABSTRACT

Reagents of biological origin are becoming more and more important in the field of metallurgy, especially in the areas of mineral processing and hydrometallurgy. The advantage of lower operating cost over physical and chemical processes and the capacity to operate with low grade ores make the microbial processes further attractive. In this paper, the role of microbes directly as a reagent and microbially produced reagents or secreted metabolites in mineral processing and hydrometallurgy will be discussed. Adhesion of microbes to surfaces is known to alter the hydrophobicity of minerals. Applications include surface modification to impart hydrophobicity or hydrophilicity on sulfide or non-sulfide minerals and dissolution of precious metals. Microbes can also perform the role of flocculating agents. Biosorption of toxic and heavy metal ions by microbes are finding application in treating tailing ponds. Mechanisms associated with the use for microbially produced reagents are discussed along with some recent results.

INTRODUCTION

The ever increasing demand for the metals on the one hand and the decreasing availability of resources on the other are stimulating work across the world to look for better reagents and new techniques for the processing of low grade ores. What is expected of these reagents is better selectivity with respect to the collector, the depressant, the activator or the modifier property. Reagents of biological origin are of interest in this regard since they do have specific natural interactions with minerals. Microbes, their debris, and the secreted metabolites can act as reagents in mineral processing and hydrometallurgy due to direct or indirect interaction with minerals. Direct interaction involves adhesion or attachment to minerals, and thereby modification of the surfaces. Indirect interaction refers to the biological products acting as surface active reagents. These interactions can cause changes in the hydrophobicity of the minerals and, in the case of fine particles, dispersion or flocculation of their suspensions. Also, toxic and heavy metal ions in tailing ponds, ground and surface waters can be removed by microbes due to biosorption/bioaccumulation processes. Purpose of this review is to discuss recent microbial-based processes and technologies for mineral beneficiation and extraction.

In this review, a critical discussion of the available literature is conducted with special
reference to the following aspects.

i) Microbially induced flotation processes

ii) Secreted metabolites as flotation reagents

iii) Biosorption of metal ions by microbes

MICROBIALLY INDUCED FLOTATION PROCESSES

Søljenken and his group (1976, 1979) were the first to report the use of microorganisms of the type sulfate reducing bacteria (SRB), microbe fat and biomass in the flotation of several sulfide and nonsulfide minerals. SRB was found to depress the flotation of both chalcopyrite and sphalerite but not those of molybdenite and galena (Figure 1) (Søljenken, 1976). Studies with different sulfide concentrates show that SRB can desorb xanthogenate coatings causing them to lose their flotation activity. In the case of bulk concentrates containing both sphalerite and galena, although control experiments do not show any selectivity in their separation, treatment with SRB yielded about 95% recovery of galena while sphalerite recovery under these conditions was only 4.5%.

*Thiobacillus ferrooxidans* is the most widely studied bacterium and is currently the major leaching microorganism of economic importance. *T. ferrooxidans* can directly oxidize sulfide minerals through prior bacterial attachment or indirectly through ferric sulfate generated as a metabolic product (Bryner et al, 1954; Berry and Murr, 1978; Berry et al, 1978; Torman, 1986). Yelloji Rao, Natarajan and Somasundaran (1992 a & b) have reported the effect of bacterial conditioning with *Thiobacillus ferrooxidans* on the floatability of sulfide minerals. Figure 2 shows the effect of bacterial conditioning on sphalerite recovery under different flotation conditions (Yelloji Rao et al, 1992b). While pretreatment with sulfuric acid solution at pH 2 without any bacteria itself improved sphalerite flotation significantly with and without flotation reagents, conditioning at the same pH with *Thiobacillus ferrooxidans* (10^6 cells/ml) caused some further improvement in the floatability. However, bacterial treatment did not show any effect when flotation was carried out after conditioning with both the activator (CuSO₄) and the collector (sodium isopropyl xanthate). It is also shown that when the cell dosage was increased to 10^9 cells/ml, the floatability of sphalerite was reduced drastically, even when the flotation was carried out after conditioning with the flotation reagents (Yelloji Rao et al, 1992b). In the case of galena also, natural floatability was enhanced appreciably upon pretreatment with sulfuric acid solution (Figure 3) (Yelloji Rao et al, 1992b). However, when *Thiobacillus ferrooxidans* (10^6 cells/ml) was also used for the conditioning, the

**Fig. 1. Effect of conditioning with sulfate reducing bacteria on sulfide flotation**

**Fig. 2. Effect of conditioning with *Thiobacillus ferrooxidans* on sphalerite flotation**
enhancement of natural floatability obtained was minimal. The floatability of collector treated galena was reduced by biopretreatment and an increase of cell dosage to \(10^9\) cells/ml further depressed the flotation drastically.

During the conditioning with sulfuric acid solution, dissolution or surface oxidation of the mineral is possible.

\[
\text{ZnS} \rightarrow \text{Zn}^{2+} + S + 2e^{-} \quad (1)
\]

\[
\text{PbS} \rightarrow \text{Pb}^{2+} + S + 2e^{-} \quad (2)
\]

Elemental sulfur thus generated on the mineral surfaces is hydrophobic and hence can increase the natural floatability of both sphalerite and galena. *Thiobacillus ferrooxidans* is known to oxidize such elemental sulfur to sulphate (Bryner et al., 1954). While the zinc sulfate formed on the sphalerite surface is soluble at the acidic pH of 2, lead sulfate species formed on the galena is insoluble. Oxidized insoluble products on the sulfide mineral surface are known to interfere with the action of collector (Wark, 1938). The flotation of galena was hence significantly decreased upon biopretreatment. At the high cell dosage of \(10^9\) cells/ml, floatability is proposed to be governed mainly by the enhanced attachment of the bacteria.

Lyalikova and Lyabavina (1986) have discussed the possibility of using *Thiobacillus ferrooxidans* to separate antimony and mercury sulfides by flotation. Bacterial conditioning for ninety minutes produced no change with respect to cinnabar recovery (89%) while antimonite recovery decreased from 89% to 62% leading to almost complete separation. It is suggested that *Thiobacillus ferrooxidans* can oxidize the surface of antimonite crystals leading to depression of the floatability while cinnabar remains unaffected with no change in its floatability.

In contrast to the above in fuels area there is a dire need currently for advanced coal cleaning processes to treat pyritic sulfur coals in an environmentally acceptable and cost effective manner. Townsley et al (1987) have reported the effects of bacterial conditioning with *Thiobacillus ferrooxidans* on the suppression of pyritic sulfur as a part of the cleaning process. The effects of conditioning pyrite with bacterial suspension in direct bacterial liquor, membrane filtered liquor with and without bacteria at pH 2.0 are illustrated in Figure 4 (Townsley et al., 1987). The natural floatability of 84.5% was found to decrease to about 7.7% upon conditioning of with bacteria suspended at pH 2 for 2.5 minutes. Best suppression was
obtained with membrane filtered liquor supplemented with bacteria wherein the recovery was only 4%. This clearly shows the importance of bacteria and the associated medium in altering the floatability of pyrite. Attia and Elzeky (1985) have shown that at natural pH, neither the nutrient medium without bacteria nor the bacterial suspension produced any depression of coal (Figure 5). In the case of pyrite, although nutrient medium alone did not affect flotation, bacterial conditioning was found to affect the flotation and such an effect was severe when old culture was used.

Different mechanisms have been suggested for pyrite suppression due to bacterial conditioning. Townsley et al (1987) have proposed it to be due to changes in surface charge in response to either adsorption of intact bacteria, bacterial metabolites or bacterial debris. Harada and Kuniyoshi (1985) have attributed pyrite depression to bacterial oxidation causing the formation of jarosite or a jarosite-like insoluble sulfate (hydrophilic film) on the pyrite surface. Attia and Elzeky (1985) have pointed out that the bacteria could adsorb on the mineral surface in this case and grow. Also, *Thiobacillus ferrooxidans* are capable of producing polymeric surface active substances (mainly polysaccharides and lipids) which can adsorb on the pyrite surface. Bacterial growth coupled with adsorption of cell-excreted compounds can be expected to make the mineral surface more wettable and thus affect its floatability. The bioadsorption process is believed to be rapid enough to be completed in a matter of few minutes. In fact, in the case of pyrite, Bagdigan and Myerson (1986) observed 90% of the inoculated cells to become attached to the surface within two minutes of conditioning. Work on pyrite flotation has shown that a short conditioning for 2.5 minutes with *Thiobacillus ferrooxidans* can depress the natural floatability (Townsley et al, 1987). It is unlikely that within such a short period enough bacterial metabolites are produced to affect the floatability to a measurable extent. The other possibility then for flotation depression under these conditions is the bacterial attachment onto the minerals which will result in a hydrophilic surface.

Dogan et al (1985) have reported that bacterial conditioning with *Thiobacillus ferrooxidans* followed by flotation not only removed pyritic sulfur more than by bacterial leaching alone but also resulted in a coal with a lower ash content. However, the reasons for the removal of ash content as well as the removal of pyrite due to bacterial conditioning are not known.

### BIOMODIFICATION OF NONFERROUS AND NONSULFIDE MINERALS

Microbial products such as secreted metabolites, microbe fat and biomass can also act as flotation reagents. Solojenken (1979) has demonstrated the use of reagents of biological origin such as microbe fat and biomass as flotation reagents for nonsulfide and fluorspar ores of different origin. Good selectivity was obtained with microbe fat as a collector for the flotation of fluorspar; associated minerals, calcite and barite, floated little and quartz practically did not float. Optimum flotation of fluorspar with oleic acid, a conventional collector for nonsulfide ores, is obtained in the pH range of 7 to 10 while with microbe fat the range is 4 to 10. The expanded pH range is considered to result from the fact that microbe fat contains a number of saturated and unsaturated fatty acids with the former attaching rapidly to the fluorite surface. Infrared spectra for the collector and the microbe fat interactions with minerals were identical.
The use of biomass as a flotation agent has been demonstrated also for celestine and associated minerals, calcite, barite and quartz (Figure 6) (Solojenken, 1979). Both calcite and barite were depressed with 10 mg/l of biomass while about 20% of celestine could be selectively floated. Increase of biomass concentration further increased the selectivity. With about 50-75 mg/l, all the associated minerals were practically depressed. Solojenken (1979) further compared the depressing action of biomass with that of dextrine, a conventional depressant. With 300 g/ton of dextrine, 96.2% CaF₂ with 84.9% recovery was obtained; in comparison with 96.3% of CaF₂ with a recovery of 86.5% obtained with 50 g/ton of biomass. The ability of biomass macromolecules to hydrate in aqueous solution and to more selectively adsorb on the gangue minerals made them potential depressors in nonsulfide ore flotation.

**BIOSORPTION OF METAL IONS BY MICROBES**

Microorganisms are employed for recovering metals from solid wastes in two ways: extraction of metals from insoluble solids by microorganisms through bioleaching and recovery of metal ions from solutions by microorganisms through biosorption/bioaccumulation. The latter process is also used to concentrate metals from effluents before discharge to streams, lakes or ground waters to minimize accompanying pollution problems. In the past two decades, research on biosorption has advanced from fundamental to applied stage owing to its application for environmental protection and the economical advantage over conventional chemical processes. Generally metal ions are present in the effluents in dilute concentrations and do not pose any immediate danger. However, the metals can get concentrated by microorganisms due to the persistence of former in the environment and their sorption can become detrimental to microorganisms when the concentration of the metal ions exceed the tolerance limits.

There are reports in literature on biosorption of almost all heavy metal ions which are hazardous to humans and animals (Tsezos and Volesky, 1982; Ahlf, 1988; Kuyukak and Volesky, 1989a & b; Scharer and Byerley, 1989; Tsezos et al, 1989; Ralph, 1985). Adsorption by the bacterium *Cyanidium caldarium* of heavy metal ions which include Cd²⁺, Co²⁺, Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ has been demonstrated by Ahlf (1988). Also, extensive work has been done by Kuyukak and Valesky (1989a and b) on the accumulation of cobalt by marine alga and the mechanisms involved.

Mechanisms associated with the adsorption of ions by microorganisms and immobilized biomass are discussed below with special reference to uranium. Isotherms for biosorption by *A. vinelandii* at various pH values from uranyl nitrate solutions containing 2.4 g l⁻¹ sodium sulfate are shown in Figure 7 (Scharer and Byerley, 1989). Also shown are the two isotherms obtained with young and old cultures under the same physiological conditions. The observed difference was attributed to the reduced amount of capsular slime in older cultures. Surface properties such as zeta potential and hydrophobicity have been shown to depend, in addition to added inorganic and organic species, on such treatments as aging, or freeze/thaw (Yelloji Rao et al, 1993). This indicates the importance of controlling the harvesting conditions in sorption processes. Studies carried out by Scharer and Byerley (1989) with capsular polysaccharides extracted from plasmid transformed bacteria have shown algal alginate to possess higher uranium sorption capacity than the whole cells (Scharer and Byerley, 1989). Since neither the biomass nor the polysaccharides displayed significant selectivity for uranium, it was proposed that the ions could bind to carboxylic residues of the biopolymers. A pilot plant study of the immobilized biomass of *R. arrhizus* for the recovery of uranium from the bioleach solutions has shown that the biomass can be effectively used for 12 cycles with consistent performance thus showing promise for upgrading the process to industrial levels (Tsezos et al, 1989).

**CONCLUDING REMARKS**

Reagents of biological origin can drastically alter the surface properties of the minerals. Such changes can be exploited to separate minerals during flotation for the purpose of beneficiation and
for the cleaning of coal. Uptake of metal ions by the microbes and the biomass can also be used for the removal of hazardous heavy metal ions. Flocculation as well as dispersion, for example, for waste treatment, can also be achieved by biological processes but mechanisms involved are not well understood in this case. The cells can produce extracellular polysaccharides and polypeptide based polymers, which have the capacity to function as flocculating agents. The biopolymer segments can bridge not only the cells but also fine mineral particles. Microbial adhesion to minerals although in many cases appears to depend on the specific property of the fimbriae present on the cell surface, adhesion does occur in their absence as well. Presence of fimbriae as well as their removal has been recently shown to alter key surface properties of the microbes (Yelloji Rao et al., 1993).

Although, preliminary studies on microbial interactions with minerals indicate some potential applications, for full exploitation of all the biological processes and for scaling up to large reactors, more information on factors that control microbe-mineral interactions, such as, role of fimbriae, effective permeability for the flow of nutrient/culture medium in the particle bed, microbial tolerance to high temperature and concentrations, design and optimization of the rate of biological processes and cost effectiveness is necessary. Genetic manipulation can be used to make microbes adapt to elevated temperatures, metal ion concentrations and extreme pH conditions. Wide use of microbes or their production on an industrial scale can be expected to occur with improvement in process efficiency and cost.

REFERENCES

Berry, V.K. and Murr, L.E., 1978. Direct Observations of Bacteria and Quantitative Studies of their


