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Technical note

Reagents in calamine zinc ores flotation

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Abstract

Oxidised zinc ores are traditionally floated with fatty amines as collector. The effectiveness of this reagent requires a pre-sulphidisation stage with sodium sulphide in conjunction with soda ash. Especially in the case of calamine ores, a dispersing agent becomes necessary. The collector must be emulsified with a fuel oil and the frother. This flotation system is characterised by the use of very large amounts of reagents. The proportion of each reagent in the reagents system must be carefully optimised.

Keywords: Froth flotation; Flotation reagents; Flotation activators; Flotation collectors

1. Introduction

The production of zinc concentrates from oxidised ores is still relevant in countries such as Brazil, Namibia, Iran, and Australia, even after the pioneering mines in Italy (Sardenia) and France were shut down. The technological development for processing calamine ores (major zinc bearing mineral hemimorphite) occurred after the second world war and until the seventies Italy and France lead the investigations on this subject. After the depletion of their reserves, research work on this field slowed down.

The Brazilian company producing zinc concentrates operates an underground mine producing a willemite ore (fresh ore) and an open pit mine producing hemimorphite or calamine ore. The concentrator operates different circuits for each ore type. The flotation of the willemite ore is performed with the following reagents scheme: pre-sulphidisation with sodium sulphide and flotation with primary amine as collector. The flotation feed is not deslimed and the circuit yields zinc grades of 44% and recovery levels of 87%. The calamine ore (weathered ore) requires desliming in hydrocyclones and yields poor results, zinc grade reaching 38% and the recovery level staying at 55%. A polyacrilate polymer is utilised as gangue dispersant/depressant in the calamine circuit.

The demand for zinc in Brazil is increasing steadily. In order to reduce the production deficit, this laboratory scale investigation aimed at contributing to enhance zinc recovery by means of a more effective dispersion and the use of adequate reagents combinations and dosages for the flotation of calamine ore slimes. The dispersion of the mineral particles in the pulp is crucial for increasing the flotation selectivity of these ores. The characterisation studies provided an explanation for the differences in flotation performance between calamine and willemite ores. The results achieved will be useful for plant operators and researchers dealing with other zinc ores bearing calamine as the major zinc mineral.

2. Characterisation

The undeslimed calamine ore was characterised, on a semi-quantitative basis, by X-rays diffraction. The major

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minerals detected were quartz, hemimorphite, dolomite, goethite, and biotite. The minor minerals detected were, chlorite, calcite, whitherite, cerusite, sphalerite, tremolite, smithsonite, hematite, siderite, apatite, felspar, magnesite and zincite.

It is worthwhile stressing that 45% of the ore is bellow 38 μm, and the zinc content in this fraction is 10.5%, representing a distribution of 44.3%. The challenge of floating this material is crucial for improving zinc recovery in the calamine circuit.

Both ores, willemite and calamine, were analysed in a BET apparatus. The willemite ore presents specific gravity 3.3, pores mean diameter 115 Å, external surface area 2.16 m^2/g and micropores area 0.25 m^2/g. The calamine ore presents specific gravity 3.0, pores mean diameter 96 Å, external surface area 7.74 m^2/g and micropores area 0.51 m^2/g. The poor flotation performance of the calamine ore in comparison with the willemite ore might be at least partially explained by the much larger external surface area and micropores area. Billi and Quai (1963) and Luz and Baltar (1982) verified that the conditioning time for hemimorphite should be twice that for willemite, emphasising the importance of the surface characteristics.

The isoelectric point of a hemimorphite sample, as pure as possible, collected in the open pit mine, was determined by three techniques: Mular and Roberts (1966) method, and electrophoretic mobility in a Rank Brothers apparatus and in a Micromeritics apparatus. The observed pH values for the IEP were: Mular and Roberts 6.9; Rank Brothers 5.4; Micromeritics 6.2. The Rank Brothers apparatus is probably more sensitive to the impurities present in the sample. In this technique a large variability in the velocities of the particles selected for observation was detected. The Micromeritics apparatus principle is the determination of the mass of the samples that migrate to the cell, which is compared with the total mass, rendering the technique more representative for less pure mineral samples.

3. Dispersion

The dispersion degree of the slimes of the calamine ore was determined in a sedimentation tube, described by Galéry (1984).

The statistic tool of two levels replicate complete factorial design was employed to evaluate the individual effect of the variables: dispersing agents, sodium sulphide, pH, and reagents addition sequence. These results were treated with the help of the Yates algorithm and optimised by means of the ascending path method leading to the optimisation of the dispersion degree. Calgon (commercial product combining sodium salts of cyclic hexametaphosphoric acid and linear dimeric pyrophosphoric acid), analytical grade sodium hexametaphosphate, sodium polyacrylate (trade name; dispersol 589) and carboxymethyl cellulose (CMC) were used as dispersants. Sodium sulphide was added in all tests. Despite the good performance of sodium silicate in the flotation tests, this reagent was uneffective in dispersion experiments, so it was not included in the statistical design.

An analysis of results including the interactions of significant variables indicated the following remarks:

(i) the dispersion degree of the slimes increases significantly when the concentration of sodium sulphide changes from the low level to the top level;
(ii) sodium hexametaphosphate is the most effective reagent regarding an increase in the dispersion degree; this reagent presented good performance in another investigation with a different calamine ore from the same region (Peres et al., 1994);
(iii) the interaction between hexametaphosphate and sodium sulphide reduces the dispersion degree; the same effect is observed in the interaction between polyacrylate and sodium sulphide;
(iv) sodium polyacrylate acted as a slimes dispersant but it was not as effective as sodium hexametaphosphate;
(v) Calgon is also an effective dispersant;
(vi) the interaction between hexametaphosphate and Calgon caused a decrease in the dispersion degree when the variables change from the low to the high level;
(vii) the association between polyacrylate and Calgon decreases the dispersion degree when the concentration of these reagents increases.

The ascending path method lead to the definition of reagents dosages that yield improved dispersion degree conditions: [Na_2S] = 500 g/t; pH = 10.5; [sodium hexametaphosphate] = 3000 g/t.

4. Flotation

The investigation was initially directed towards the flotation of the slimes fraction of the calamine ore. The performance of several batch column flotation experiments was consistently extremely poor. A decision was made to concentrate the efforts on the flotation of the undeslimed calamine ore, a procedure similar to that adopted in the willemite industrial circuit.

Sulphidisation is the first step towards the successful selective flotation of oxide zinc ores. In the pH range relevant to the present investigation (8.0–11.5) HS^- is the predominant species from sodium sulphide (Brookins, 1988). HS^- adsorbs onto the calamine surface, rendering its surface charge more negative (Salum et al., 1992; Raffinot, 1970).

Excessive dosages of sodium sulphide impair the flotation selectivity and the pulp dispersion. The adequate dosage for the undeslimed calamine ore stays in the range from 3000 to 5000 g/t. At approximately pH 12, coagulation of particles in the pulp is observed.

The selectivity of calamine flotation may be enhanced by means of combining sodium sulphide with sodium carbonate (soda ash). For the same zinc recovery (65%), zinc grade decreased from 20.0% to 15.6% when the Na_2S/Na_2CO_3 ratio was changed from 68.0/32.0 to 85.5/14.5. The improved selectivity in the presence of sodium carbonate was reported by Caproni et al. (1979), in an investigation concerning the last calamine reserves in Sardinia.

Among the gangue depressants selected for the investigation (corn starch, dextrine, CMC, sodium silicate and potassium di-cromate), CMC and sodium silicate were slightly more effective. In general, the presence of depressants did not improve significantly the flotation selectivity.

Despite the superiority of sodium hexametaphosphate in comparison with sodium silicate in the dispersion experiments, the latter was more effective in the flotation tests due to its capability to promote a selective dispersion in the system, leading to a low dispersion degree of dolomites, enhancing its depression, a feature reported by Galéry (1984). According to Shin and Choi (1965) the maximum adsorption of sodium silicates onto calcium minerals occurs at pH 9.8, $HSiO_3$ being suggested as the active adsorbed species.

The usual plant practice of calamine flotation involves pH levels close to 12, modulated with sodium sulphide and soda ash. The emulsification of amine with fuel oil or kerosene and MIBC (frother) render the flotation process feasible at lower pH levels. The required amount of sodium sulphide, necessary to promote selectivity among the different minerals (especially silicates) present in the ore, is the relevant aspect, rather than the pH value itself. The role of the fuel oil, as an amine chain extender, was firstly reported by Taggart, 1945, who mentioned that its presence renders unnecessary the pH control. due to an increase in the mineral/air bubble contact angle, keeping this contact at the surface, a relevant feature in the case of an ore with high porosity degree such as calamine. The success of the use of fuel oil relies on the preparation of an emulsion primary amine/diesel oil/MIBC at the ratio 1:0.16:0.4. The adequate dosage range for this emulsion is from 500 g/t to 800 g/t.

An industrial flotation test, performed with undeslimed calamine ore, under adequate dispersion condition, lead to the outstanding result of 75.8% zinc recovery, at 37.4% zinc grade, representing 20% increase in zinc recovery.

5. Conclusions

The willemite ore presents external surface area of 2.1610 m^2/g and micropores area of 0.2534 m^2/g, while the calamine ore presents external surface area of 7.7421 m^2/g, micropores area of 0.5068 m^2/g.

The larger surface area of the calamine ore justifies the requirement of larger reagents consumption, as well as the preparation of an emulsion primary amine/diesel oil/MIBC. The use of the emulsion at an adequate dosage increases the zinc recovery and decreases the sodium sulphide consumption.

The combination of sodium sulphide with soda ash at the ratio 68%/32% enhances dolomite depression and also chemically stabilises the sodium sulphide.

Dispersion is the key factor for the successful flotation of calamine zinc ores. The association between sodium silicate and sodium hexametaphosphate (50% each) at the dosage of 7000 g/t is adequate to enhance the flotation performance.

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