



ORIGINAL ARTICLE

Carbonate Content Reduction in Zinc Ore Concentrate

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The hydrometallurgical zinc extraction from the willemite concentrate is impaired by the presence of high carbonate content. A stiff froth is produced causing zinc losses and acid consumption. A standard procedure was developed to define the acceptable froth layer height in a laboratory test. Froth layers shorter than 2 cm resulted from carbonate content in the concentrate below 10.8%. The feasibility of adding a carbonate flotation stage to the circuit was tested in laboratory and pilot scales. Among the collectors investigated, only those presenting a saponification degree above 189 mg KOH/mg were effective in the laboratory experiments. Oleine and rice bran oil soaps were selected for the pilot scale experiments. The final stage was a one month long industrial trial performed in a circuit consisting of three pneumatic cells G18. A comparison between the average results of the industrial trial including the carbonate flotation stage and data of the raw industrial concentrate indicated that the MgO content in the concentrate dropped from 3.7%-3%. Concurrently, the carbonate content in the concentrate dropped from 11%-10.6%, the zinc grade in the concentrate increased from 41.4%-42% and the zinc recovery increased from 86.6%-89.8%. The concentrate was processed in the hydrometallurgical plant with no frothing problems.

KEY WORDS: Flotation froth; Flotation collectors; Flotation reagents

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1. Introduction

Votorantim uses a unique autoclave acid leaching process in the production of zinc from a willemite ore concentrate. The presence of carbonates, especially dolomite, in the zinc concentrate strongly impairs the hydrometallurgical operation due to high acid consumption and the production of an extremely stiff froth that causes significant zinc losses and renders the pulp handling very difficult. Three routes were tested in laboratory and pilot scale aiming at reducing the carbonate content in the zinc concentrate: ore sorting and

heavy media separation as pre-concentration stages, and reverse carbonates flotation from the zinc flotation concentrate. Technical economical analysis pointed towards the industrial implementation of the last route.

The inexistence of references in the technical literature addressing the selective flotation between willemite and dolomite directed the literature review to the phosphate ore concentration, with emphasis on the selectivity between apatite and carbonates. Regarding either industrial practice or laboratory investigations, reports on carbonate depression significantly surpass those on reverse carbonate flotation. According to Prasad *et al.*^[1], 75%-80% of the low grade world phosphate reserves are associated with carbonate gangue. Henchiri^[2] developed a carbonate flotation pro-

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cess, preceding the phosphate flotation, using as collectors mono and diphosphoric esters containing propylene oxide. Sulphuric acid, sodium fluorsilicate, and starch were used as phosphates depressants. The pulp was heated to 40 °C to enhance the selectivity.

Prasad *et al.*^[1] developed a reverse anionic flotation scheme in two stages, using sodium oleate as a carbonate collector and orthophosphoric acid as an apatite depressant. The same collector was utilised by Abramov *et al.*^[3], the flotation being performed at pH = 6.3, modulated with phosphoric acid.

Lima^[4] compared the anionic direct flotation of the Brazilian Cajati's ore with the double stage flotation; the second stage consisting of reverse carbonates flotation. The advantage of the second scheme was the production of two concentrates. The phosphate concentrate was used by the fertiliser industry, while the carbonates concentrate was used in cement manufacture.

Investigation by Zheng and Smith^[5] revealed that carboxymethylcellulose, citric acid, and naftil-nathyl sulphonates are effective in dolomite depression, without significant interference in apatite flotation. Oliveira^[6] corroborated the selective depressant action of carboxymethylcellulose on dolomite.

El-Midany *et al.*^[7] suggested a different route for the separation between carbonates and phosphate. The carbonates solubility under slightly acidic solutions generates CO₂ micro bubbles at the mineral/aqueous phase, producing a stable dolomite-bubble that levitates at the cell. This condition is similar to that occurring at Votorantim's hydrometallurgical plant, where the micro bubbles generated in the autoclave, in contact with the fine willemite particles, rendered hydrophobically by the collector, form a persistent, thick, and well-drained froth that accumulates at the top of the thickener.

2. Materials and Methods

The samples for the laboratory scale flotation tests were collected at Vazante's concentrator: (i) flotation circuit feed; (ii) flotation's circuit concentrate, designated as raw concentrate. The experiments were performed in an Outokumpu batch flotation machine operated at the conditions: froth layer height of 5 cm; air pressure of 8 kgf/cm²; water flow rate equals to 2.8 L/min; pulp volume of 4.0 L; percentage of solids of 34% (feed); and 25% (raw concentrate). Fatty acids from different international and local manufacturers were selected for this preliminary stage: MDB969, MDB970, MDB971 (Akzo Nobel); hidrocol (Hidroveg); ACC20,

AGCC10, AGCC50 (AG Aditivos); rice bran oil (Almad, Braido, Aboisso, Irgovel); oleine (Casquimica); PIETFLOAT LA01, PIETFLOATLT01, PIETFLOAT LD131A, PIETFLOATLD132A, R&DSORI, R&DRI, R&DOL, R&DLA01-SE, R&DSE, R&DOLSE, R&DSSOR (Pietsch Chemicals).

Sodium silicates manufactured by four companies were tested as willemite depressant. MIBC was utilized as frother. The fatty acids were saponified with caustic soda and the reaction extent was monitored to keep a level close to 75%.

A standard procedure was developed to compare the frothing level produced by the acidic leaching of the raw willemite concentrate and that of the concentrate submitted to further carbonate flotation. Concentrates yielding froth levels of heights below 2 cm are considered adequate for the hydrometallurgical plant practice.

Based on their low frothing production capability, two collectors were selected for the pilot scale stage: oleine (fatty acids compound containing approximately 55% oleic acid) and rice bran oil soaps. Votorantim's pilot plant is a continuous operation facility capable of handling 200 kg/h-300 kg/h, equipped with two rougher (70 L), four scavengers (35 L), and one mechanical cells cleaner (35 L).

The industrial trial was performed in a circuit consisting of three gyratory cells G18, known as G cells (Pneumatic Flotation Technology Imhoflot). The industrial trial lasted one month. A blend of oleine and rice bran oil soaps (300 g/t) and sodium silicate (4,000 g/t) were used, respectively, as collector and depressant/dispersant.

3. Results

The results presented in Table 1 show that the raw concentrate weight partition at 20 mm indicates similar undersized and oversized fractions, but zinc concentrates in the coarse fraction and calcium and magnesium (present in dolomite) in the fine fraction. The species distribution suggests that the industrial carbonate flotation should be performed in a machine designed to recover fine particles.

A target of carbonates content in the willemite concentrate no higher than 10.8% was established based on the froth generation in the hydrometallurgical plant.

The laboratory scale test work revealed that the key factor for reaching the proposed target was the collector saponification degree expressed in mg KOH/mg of the reagent. The reverse carbonates flotation yielded willemite concentrates with carbonates content below 10.8% when the collector saponification degree reached at least 189.

Table 1 Grades and distribution of species in the raw concentrate +20 µm and -20 µm fractions

Fraction (µm)	Weight %	Grade %					Distribution %				
		Zn	Fe	CaO	MgO	SiO ₂	Zn	Fe	CaO	MgO	SiO ₂
+20	49.4	49.1	4.49	3.04	2.51	28.2	56.3	35.0	35.3	33.5	54.5
-20	50.6	37.3	8.15	5.46	4.86	23.0	43.7	65.0	64.7	66.5	45.5
Calculated	100	43.1	6.34	4.26	3.70	25.6	100	100	100	100	100
Analyzed		43.1	6.26	4.62	3.86	24.3					

Saponified oleine (rich in oleic acid) and rice bran oil (rich in oleic and linoleic acid) collectors presented saponification degrees close to the reference values of 200 and were the most effective reagents to float carbonates.

Fig. 1 illustrates the results of acidic leaching of Vazante's raw concentrate showing very high levels of froth, above 5 cm, in the laboratory frothing standard test. Fig. 2 illustrates the results of the test using Vazante's concentrate produced in the circuit with carbonates flotation with five collectors presenting high saponification degrees. The achieved froth heights, below 0.6 cm, are adequate for the hydrometallurgical extraction stage.

The results of the pilot scale tests are summarized in Table 2.

A blend of oleine soap and rice bran oil soap was selected to be utilized as collector in the industrial trial. The use of collector blends to improve selectivity and recovery is common practice in flotation plants. Barros *et al.*^[8] and Lima and Peres^[9] reported that blending the traditional collector rice bran oil soap with a synthetic collector (sulphosuccinamate) improved the flotation selectivity of a grainy phosphate ore. Araujo *et al.*^[10] mentioned that the conjunction of ether amine and fuel oil is widely employed in phosphate flotation in Florida and was used in iron ore flotation in Brazilian concentrators.

A comparison between the average results of the industrial trial including the carbonates flotation stage and data of the raw industrial concentrate indicated that the MgO

Table 2 Pilot scale flotation tests: comparing blank test (no carbonate flotation) and carbonates flotation with oleine and rice bran oil soap

Pilot scale test	MgO %	Carbonate %	Zn recovery %
Blank	3.35	11.0	86.71
Carbonate flotation oleine soap	3.01	10.3	88.24
Carbonate flotation rice bran oil soap	2.85	9.9	91.36

content in the concentrate dropped from 3.7%-3%, the carbonate content in the concentrate dropped from 11%-10.6%, the zinc grade in the concentrate increased from 41.44%-42%, and the zinc recovery increased from 86.6%-89.8%.

The froth product of the carbonate flotation stage represented 3% in weight, with 30% zinc content, and was sold to micronutrient companies.

4. Conclusions

The presence of carbonate content above 10.8% in the willemite concentrate resulted in stiff froth production in the hydrometallurgical zinc extraction operation. A laboratory standard procedure was developed and the acceptable froth layer height was defined as 2 cm.

Laboratory scale tests indicated that carbonates could be floated from the raw concentrate with collectors presenting saponification degree above 189 mg KOH/mg of the reagent.

Oleine and rice bran oil soaps were successfully tested in a continuous pilot plant. A blend of oleine and rice bran oil soaps was used as carbonate collector in an industrial trial in a circuit consisting of contact cells, yielding a concentrate with average carbonate content of 10.6%, acceptable for the hydrometallurgical plant operation.

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Fig. 1 Froth level of tests with the raw concentrate, froth layer height >5 cm

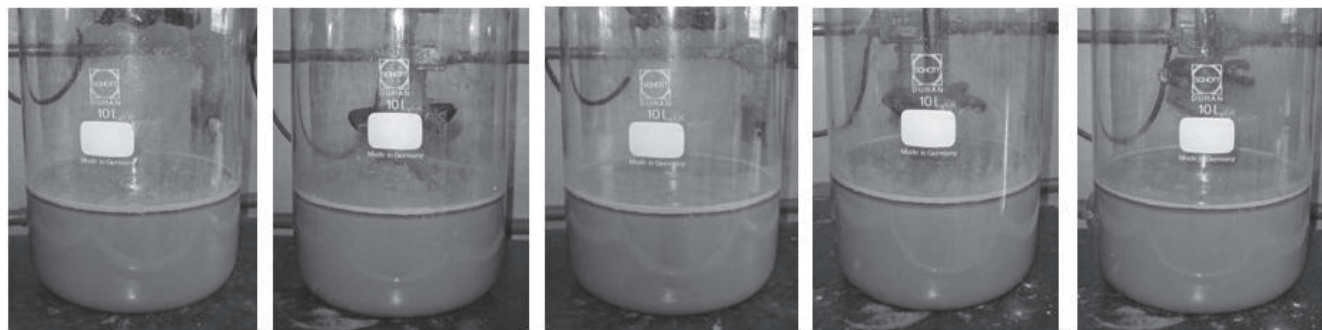


Fig. 2 Froth level of tests with the concentrate submitted to carbonates flotation with different collectors, froth layer height <0.6 cm

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