



# Simultaneous removal of calcium and sulfate ions from flotation water of complex sulfides



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## ABSTRACT

This paper presents and discusses the results of an experimental study designed to investigate the feasibility of removing calcium and sulfate from saturated solutions by using calcium aluminate-based compounds. The results obtained show that the treatment of saturated solutions (0.016 mol/L  $\text{CaSO}_4$ ) alkalized at pH above 12 by adding 0.75 g/L CaO and treated with a calcium aluminate-based compound (C70: 70%  $\text{Al}_2\text{O}_3$ , 30% CaO), promotes the precipitation of calcium sulfate as ettringite, which is a hydrated calcium sulfoaluminate, in equilibrium with residual calcium and sulfate concentrations below 200 mg/L. The active species of compound C70 is the monocalcium aluminate ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), which is the responsible of promoting ettringite precipitation. The use of a large excess of monocalcium aluminate significantly increases the removal kinetics but has the disadvantage that the excess is eventually hydrolyzed releasing calcium and aluminate ions to the solution. It was also observed that an excessively long contact time (e.g., 50 h), results in the acidification of the suspension due to absorption of atmospheric  $\text{CO}_2$ , causing the dissolution of the ettringite, which is stable at pH above 11.5. The best experimental conditions observed are the use of a slight excess of reactants (with respect to the stoichiometrically required): 0.75 g/L CaO and 2 g/L of C70 and a reaction time of 6 h.

## 1. Introduction

Management of water resources has become a very important subject in the economic development of countries, since this resource is directly related to the quality of life and the environment. For this reason, the reuse of water in industrial activities is a common practice in most countries, including those where water scarcity is not a current problem. In this context a series of investigations have been developed focusing on the treatment and use of recycled water in mineral processing, with the aim of minimizing the use of fresh water in the mining industry. In the particular case of complex sulfide flotation, the recycled water must be appropriately classified, treated and stored, to be returned to the different sections of the flotation operation, according to their effect on the surface properties of sulfide minerals of interest. Such actions may increase the utilization of recycled water, resulting in a significant decrease in operating costs (Levy et al., 2001; Rao and Finch, 1989).

However, the use of recycled water in sulfide flotation operations has important effects on recovery of mineral species of interest and separation selectivity: it can promote flotation of sulfide species that are

wanted in the tails, depress species that are targeted to float or decrease selectivity in the hydrophobization of the species to be separated. Typical contaminants in recycle water are colloidal solids, base metal ions, thiosalts, sulfite, sulfate, chloride, magnesium, calcium, sodium and potassium, as well as reagents such as frothers, collectors and depressants (Bıçak et al., 2012). Generally, recycle water is recovered from thickeners and filters, so the concentration of dissolved ions and suspended solids is substantially increased (Johnson, 2003; Levay et al., 2001). Two of the ions most commonly present in the process water of complex-sulfide flotation are calcium and sulfate. The presence of calcium is due to the use of calcium oxide (CaO) to regulate the alkaline pH which is generally required, as well as to the dissolution of calcium-bearing minerals (e.g., calcite, dolomite, etc.), when present in the ore. The presence of sulfate is due to the natural oxidation of sulfide minerals, due to atmospheric oxygen in contact with the slurry during grinding, conditioning, flotation and thickening, as well as to the use of, for example, sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) as depressant of sulfide gangue. Under alkaline conditions the sulfide of the minerals ( $\text{S}^{2-}$ ) is oxidized to sulfate ( $\text{SO}_4^{2-}$ ), the highest oxidation state and the stable species (Ralston et al., 2007). Frequently, typical process waters contain

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calcium concentrations of about 750 mg/L, while the sulfate concentration may be that of the saturation for gypsum precipitation (about 1536 mg/L) or higher (Dávila-Pulido and Uribe-Salas, 2014).

The effect of calcium and sulfate on the selective hydrophobization of sphalerite and galena has been extensively studied (Bıçak et al., 2012; Dávila-Pulido and Uribe-Salas, 2014; Grano et al., 1995; Ikumapayi et al., 2012; Lascelles et al., 2013; Sui et al., 1998). It has been shown that calcium ion activates sphalerite during xanthate flotation, resulting in its recovery in the Pb/Cu flotation circuit, when it should remain in the tails (Dávila-Pulido et al., 2015); in turn, calcium sulfate at saturation concentrations for gypsum precipitation, affects the floatability of galena and sphalerite, due to the nucleation of gypsum crystals on their surfaces, which hinders particle-bubble contact (Dávila-Pulido and Uribe-Salas, 2014; Grano et al., 1995). Furthermore, it has been reported that sulfate ion adversely affects adsorption of xanthate onto galena (Ikumapayi et al., 2012; Elizondo-Álvarez et al., 2017), decreasing its flotation recovery.

In order to lessen the adverse phenomena described above, various strategies have been developed to eliminate calcium and sulfate from the process water. The most commonly used method to eliminate calcium ions from solution is based on the addition of sodium carbonate as alkalinizing agent, with the aim of precipitating calcium in the form of calcium carbonate or to dissolve the gypsum that has already precipitated on the surface of the minerals (Grano et al., 1995; Levay et al., 2001). This method deals well with the negative effect of calcium and gypsum on the hydrophobization of the sulfides of interest. However, this strategy has the disadvantage that the sulfate ion remains in the solution, which by itself is capable of affecting the adsorption of collectors on galena (Elizondo-Álvarez et al., 2017; Ikumapayi et al., 2012). However, there are methods capable of simultaneously removing calcium and sulfate from the solution, such as the SAVMIN process (Savannah Mining-Mintek, South African companies) and the CESR (Cost-Effective Sulfate Removal Process) process. Both methods have similarities such as the use of calcium oxide to achieve the required alkaline pH (greater than 11), followed by the addition of an aluminum compound, to finally obtain a solid that incorporates calcium and sulfate into its structure, decreasing their concentration in the treated solution. The main difference between the two processes, in addition to the reagent used to remove calcium sulfate, is that the SAVMIN process recycles the precipitated solid to some point into the circuit (Environmental, 2003).

There is a similar method available commercially, capable of eliminating calcium and sulfate simultaneously. This method is based on the addition of calcium oxide to achieve an alkaline pH between 11 and 13, followed by the addition of aluminum. The technology developed based on this method is marketed by the Finnish company Outotec, and consists of the precipitation of calcium sulfate as ettringite, an hydrated calcium sulfoaluminate of chemical formula  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$  (Outotec, 2014). This method is capable of dissolve precipitated gypsum and removes calcium and sulfate ions, as well as other impurities (in the form of metal hydroxides: Ni, Cd, Cu and Zn). In the present study, the main objective is to remove calcium sulfate from saturated solutions, using calcium aluminate compounds, to obtain an aqueous solution of final calcium and sulfate concentrations below 200 mg/L, which may be considered inert to the flotation performance of the sulfide minerals.

## 2. Experimental

### 2.1. Materials and equipment

The experiments were carried out in a 250 mL water-jacketed reactor, which was magnetically stirred (Thermo-Scientific). The reactor is equipped with a calcium ion-selective electrode (9720BNWP Thermo-Scientific), an electrical conductivity electrode (016010 Orion), a pH electrode (8157BNUMD Orion) and a thermometer. All experiments were carried out at 25 °C achieved by recirculating water at this temperature through the jacket of the reactor.

The measurements were carried out using saturated solutions of calcium sulfate, obtained from the supernatant of an equilibrium suspension with gypsum ( $\text{CaSO}_4\cdot2\text{H}_2\text{O}$ ) at 25 °C, which has a calcium sulfate concentration of about 0.016 mol/L. All solutions were prepared using deionized water with an electrical conductivity of about 1.5  $\mu\text{S}/\text{cm}$ . Calcium oxide reagent grade (Sigma-Aldrich) was used as alkalinizing agent and a calcium aluminate compound, termed C70, was used as precipitating agent.

### 2.2. Experimental procedure

The experiments were carried out with 200 mL of saturated calcium sulfate solution (0.016 mol/L) at 25 °C. Once the stirred solution was at the desired temperature, 0.75 g/L of CaO was added to raise the pH to about 12.5; the suspension was conditioned for 15 min to achieve dissolution and hydrolysis of the lime, in order to obtain constant measurements of the variables of interest (pH,  $\text{Ca}^{2+}$  activity and electrical conductivity of the solution). When the initial values of the parameters of interest were recorded, the compound C70 was added to initiate ettringite precipitation during which the above-mentioned variables were monitored. When the experiment was completed, the resulting solids were recovered by filtration and dried at 50 °C. These solids were characterized by X-ray diffraction (XRD, D8 Advance Bruker equipped with a copper lamp) and X-ray fluorescence spectrometry (XRF, S4 Pioneer Bruker). The clear solution resulting from the filtration was analyzed to determine calcium and sulfate concentration. During key experiments, calcium and sulfate in solution were analyzed at time intervals throughout the entire experiment. Calcium was quantified by titration with ethylenediaminetetraacetic acid (EDTA), according to the procedure reported in ASTM D511-14. Sulfate concentration in solution was determined by the turbidimetric method, according to the procedure described in ASTM D-516 02, using reagent grade barium chloride and a LaMotte 2020i turbidimeter.

## 3. Results and discussion

### 3.1. Characterization of calcium aluminate compounds

The result of the chemical analysis is presented in Table 1, where it is observed that the C70 compound mainly contains aluminum and calcium oxides ( $\text{Al}_2\text{O}_3$  and CaO, respectively) with an alumina ( $\text{Al}_2\text{O}_3$ ) to lime (CaO) ratio of 70:30% (w/w).

As shown in Fig. 1, the C70 compound mainly consists of monocalcium aluminate (CA:  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ), monocalcium dialuminate, better known as grossite (CA2:  $\text{CaO}\cdot2\text{Al}_2\text{O}_3$ ), and to a lesser extent, alumina (A:  $\text{Al}_2\text{O}_3$ ). These observations are based on the relative intensities of the characteristic peaks of the different crystalline species that make up

**Table 1**  
XRF analysis of C70 calcium aluminate compound.

Compound	$\text{Al}_2\text{O}_3$ (%)	CaO (%)	$\text{Na}_2\text{O}_3$ (%)	$\text{SiO}_2$ (%)	MgO (%)	$\text{Fe}_2\text{O}_3$ (%)
C70	71.2	27.8	0.3	0.2	0.2	0.1

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