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Comparative study on simultaneous removal of calcium and sulfate ions from flotation recycling water by aluminum hydroxide

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Abstract: Due to the environmental policies and economic reasons, the water used in some flotation operations of complex sulfide ores is recirculated, causing the ion concentration of some species to increase over time, affecting the flotation of the minerals of interest. In this work, an experimental and thermodynamic analysis of the synthetic solutions was presented with a high content of calcium and sulfate ions. The study focused on evaluating the use of two aluminum compounds for the precipitation of Ca^{2+} and SO_4^{2-} in the form of ettringite. The amorphous aluminum hydroxide was found to be more efficient than the crystalline one, giving rise to 83% calcium and 91% sulfate removal. The XRD analysis of the solids showed the main reaction product of ettringite, accompanied by small amounts of calcite, due to the absorption of atmospheric carbon dioxide. The final solution after the chemical treatment showed residual calcium and sulfate concentrations below 200 mg/L. Finally, the kinetics of calcium removal appeared to correspond to a second order reaction with respect to calcium concentration, with an apparent activation energy of 53.48 kJ/mol, which may suggest that the ettringite precipitation process is governed by the chemical reaction.
Key words: ettringite; ion removal; aluminum hydroxide; calcium; sulfate

1 Introduction

Currently, water has become an increasingly scarce natural resource and it is expected that in the coming decades it will be even more limited. To face this scenario, some companies reuse water resources in their processes, which are generally recycled from tailings dams, thickener overflows and filtration units [1,2]. However, recycle water of the complex sulfide ore operations, usually contains high concentrations of calcium and sulfate ions [3,4], which normally affects negatively the recovery of the mineral species of interest [5−10]. In order to diminish the adverse effect of these ions on flotation, several strategies have been developed to remove them from the process water [11−14].

The most commonly used method to remove calcium is based on the addition of sodium carbonate as an alkaline agent, with the aim of precipitating calcium in the form of carbonate, and dissolving the gypsum that has already precipitated and adhered to the mineral surfaces [11]. However, this strategy has the disadvantage that sulfate remains in the solution, which by itself may affect the collector adsorption on minerals such as galena [5,7−9].

The feasibility of simultaneously removing

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calcium and sulfate has been studied using compounds based on the calcium aluminate through the precipitation of ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$) (see Reaction (1)) [15−25]; however, an alkaline medium generally accomplished by the addition of lime, is also necessary to obtain the solid precipitate.

$$3CaSO_{4(aq)}+2CaO_{(s)}+CaO·Al_2O_{3(s)}+32H_2O\rightarrow 3CaO·Al_2O_3·3CaSO_4·32H_2O_{(s)} \quad (1)$$

There are alternatives to the use of calcium aluminate-based cements; one of them consists of the use of aluminum hydroxide ($Al(OH)_3$), which will provide aluminate ions to the system, completing the stoichiometry necessary to obtain ettringite.

$$3CaSO_{4(aq)}+3CaO_{(s)}+2Al(OH)_{3(s)}+31H_2O\rightarrow 3CaO·Al_2O_3·3CaSO_4·32H_2O_{(s)} \quad (2)$$

In a study by SMIT [26], the SAVMIN (Savannah Mining, South Africa) process was used to treat acid mine drainage that contained calcium, sulfate and other ions in lower concentrations. The experiments were carried out in two pilot plants, obtaining similar results in both cases, where he managed to decrease the concentration of calcium and sulfate from 475 to 50 mg/L and from 2226 to 200 mg/L, respectively. He claimed that this process is a viable option to produce water with calcium and sulfate concentrations below the potable limit, namely 200 mg/L for both ions. According to the World Health Organization (WHO) and US Environmental Protection Agency (EPA), water for human consumption should ideally contain less than 250 mg/L of sulfates [4].

JANNECK et al [22] found that crystalline aluminum hydroxide (hydrargilite)-based compounds were not appropriate for ettringite precipitation. They attributed these results to the crystallinity of the aluminum hydroxide tested, which is less reactive than the amorphous counterpart. Similarly, SAPSFORD et al [27] concluded that the crystalline properties of the aluminum species used in their study are unfavorable for the removal of calcium and sulfate as ettringite. According to the above, it is important that the aluminum compounds used in the removal of calcium and sulfate through the precipitation of ettringite are of amorphous nature.

It is worth remarking that regardless of the use of calcium aluminate (e.g., $CaO·Al_2O_3$) or aluminum hydroxide ($Al(OH)_3$), the reaction that takes place in the aqueous solution is the same, namely,

$$6Ca^{2+}+3SO_4^{2-}+2AlO_2^-+4OH^-+30H_2O\rightarrow 3CaO·Al_2O_3·3CaSO_4·32H_2O_{(s)} \quad (3)$$

In this work, we studied the treatment of saturated calcium sulfate solutions, by using aluminum hydroxide of both crystalline and amorphous nature, to precipitate ettringite, which incorporates calcium, sulfate and aluminate ions into its structure. Figure 1 illustrates that how this process could be applied in complex-sulfide flotation operations that recirculate process water from thickener/tailings dam.

2 Experimental

2.1 Materials and equipment

Deionized water with an electrical conductivity of around 1.5 μS/cm was used to prepare all solutions used. The experimental study was carried out using two aluminum hydroxide reagents ($Al(OH)_3$), with CAS numbers 21645-51-2 and 1330-44-5, a calcium aluminate cement identified as C70 provided by Almatis (cement CA-14M; 55.66% $CaO·Al_2O_3$, 39.17% $CaO·2Al_2O_3$

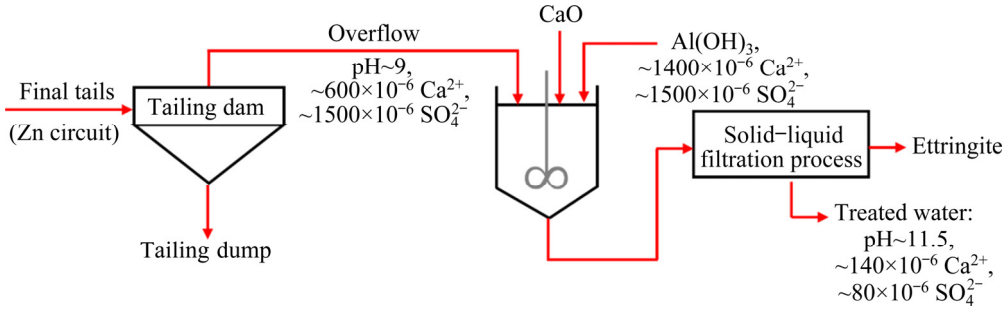

Fig. 1 Suggested process to remove calcium and sulfate in complex-sulfide flotation operations that recirculate process water from thickener/tailing dam

and 5.18% Al_2O_3 in mass fraction), and aluminum powder of particle size <75 μm. Calcium oxide (CaO) was used as the alkalinizing agent, since ettringite precipitation requires both calcium and hydroxyl ions (see Reaction (3)). All the reagents used, except the calcium aluminate cement, are of analytical grade and were supplied by Sigma Aldrich.

The test solution was obtained from a saturated solution of calcium sulfate dihydrate ($CaSO_4·2H_2O$), in equilibrium with the solid, which is filtered before being used in the experiments. The temperature of the solution is controlled by a peristaltic pump (Masterflex), which recirculates water at the desired temperature, from a digitally controlled bath (LabTech model LWB−1110), through the water jacket of a 250 mL reactor. The solution was stirred with a magnetic bar on a hotplate (Thermo-Scientific). The reactor is equipped with a calcium ion selective electrode (9720BNWP Thermo-Scientific) to monitor calcium activity, a probe to measure the electrical conductivity of the solution (016010 Orion), a pH electrode (8157BNUMD Orion) and a thermometer. The experiments were carried out at 25 °C unless another value is indicated.

The EDTA titration technique was used to determine the concentration of calcium ions, described by the D511—14 ASTM standard, while the turbidimetry technique, corresponding to the D516—02 ASTM standard, was used to determine sulfate ions concentration.

The ion removal treatment was carried out by adding aluminum hydroxide to the calcium sulfate saturated solution (0.016 mol/L), that is, ca. 640 mg/L of Ca^{2+} and 1536 mg/L of SO_4^{2-}. This concentration is similar to that typically found in complex sulfide flotation operations [11].

2.2 Hydrolyzation procedure of aluminum species

The solubility of aluminum compounds in water was studied to determine the feasibility of their use for ettringite precipitation. The experiments were carried out in an alkaline medium of pH 12, to simulate conditions of ettringite precipitation and low sulfate concentrations (see Fig. 2). 1200 mg/L CaO was used as an alkalinizing agent to obtain the desired pH (12< pH <12.5) (see Fig. 1) at room temperature. Subsequently, the aluminum compounds were added, i.e., amorphous $Al(OH)_3$, crystalline, commercial calcium aluminate (identified as C70) or aluminum powder. After 30 min, the samples were filtered, the solid precipitate was removed, and the remaining solution was acidified to keep aluminum in the solution. The filtered solutions were analyzed by means of ICP-AES (Perkin Elmer, model Optima 8300). It is important to mention that the aluminum concentration added in each experiment was the same, regardless of the aluminum compound tested.

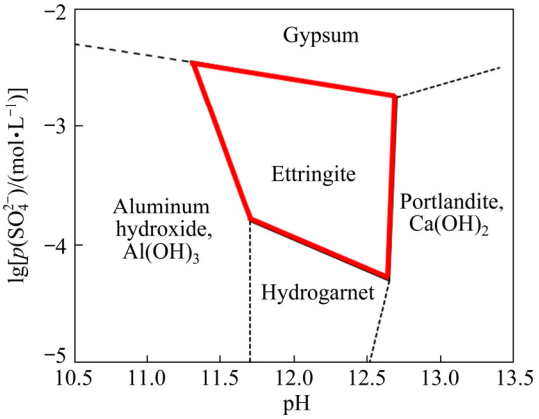

Fig. 2 Stability diagram of ettringite under alkaline media, for zero concentration of AlO_2^- (Modified from HAMPSOIM and BAILEY [28])

2.3 Characterization of reaction products

The solid product of the chemical reactions that occurred, and the remaining solid reactants initially added, were filtered, dried at room temperature and analyzed by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer. The filtered solutions were chemically analyzed to determine calcium and sulfate ions concentration.

Likewise, the reaction systems of interest were thermodynamically modeled using the HSC Chemistry V 6.1 software. This software was also used to predict the behavior of the different reactions involved in the formation of new species in the studied system.

2.4 Thermodynamic simulation of H_2O−$CaSO_4$−CaO−$Al(OH)_3$ system

The HSC Chemistry database was complemented by adding species that according to the literature, can precipitate in the reaction system, and these species are presented in Table 1. The average free energy of formation was obtained and added to the software.

Table 1 Standard Gipps free energy of formation of species that may simultaneously precipitate with ettringite, added to HSC Chemistry V 6.1 database

Species	$\Delta G^{\ominus}$/(kJ·mol^{-1})	Ref.
Ettringite	−15211±20	[29]
	−15205.9	[23]
	−15205.7	[30]
	−15202	[31]
Monosulfoaluminate $3CaO·Al_2O_3·CaSO_4·12H_2O$	−7778.5	[23]
	−7779	[30]
	−7779.8	[31]
$3CaO·Al_2O_3·6H_2O$ (Hydrogarnet)	−5014.1	[30]
	−5010.1	[23]
	−5016.9	[32]
	−5046.6	[33]
$4CaO·Al_2O_3·12H_2O$	−7326.6	[23]
	−7347.8	[30]
$2CaO·Al_2O_3·8H_2O$	−4813	[23]
	−4818	[30]
$CaO·Al_2O_3·10H_2O$	−4622	[23]
	−4618	[30]

The pH value that the simulation yields will dictate the end of the experiments since this is the main process variable that defines the stability of the precipitated ettringite (see Fig. 1). The calculations were carried out using 1 L of a saturated solution of $CaSO_4$ with a concentration of 0.0168 mol/L, corresponding to the solubility of gypsum at 25 °C, according to the HSC Chemistry software. It is worth mentioning that said solubility takes into account the effect of the ionic strength (I) of the solution, which is directly proportional to the concentration of the ionic species present in solution (see Eq. (4)), and their activity coefficients (see Eq. (5)) [34]. Therefore, the lower the ionic strength, the lower the concentration of the ions in solution, which is one of the objectives sought in the study.

$$I=\frac{1}{2}\sum_{i}^{n}(c_i z_i^2) \tag{4}$$

$$\lg\gamma=-Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}}-BI\right) \tag{5}$$

where I is the ionic strength in mol/L, c_i represents the molar concentration of the ionic species i, z_i is the valence of the ionic species i, n is the number of ionic species, γ is the activity coefficient, A and B are constants that depend on the thermodynamic temperature and at 25 °C, and they are equal to 0.51 and 0.2, respectively [35].

2.5 Optimization of thermodynamic simulation of H_2O−$CaSO_4$−CaO−$Al(OH)_3$ system

The optimization of the thermodynamic computation consisted of calculating the ionic strength of the solution using Eq. (4) and the initial concentrations of the reagents, and the corresponding activity coefficients of the ionic species using Eq. (5). These coefficients obtained were entered into the HSC software, resulting in re-computed concentrations of the species involved. This procedure was repeated until constant concentrations of the ionic species were obtained in subsequent computations.

3 Results and discussion

3.1 XRD pattern of aluminum hydroxides

The XRD characterization of the sources of aluminum hydroxide was performed to identify the phases and to determine their crystallinity. The XRD analysis results of both aluminum hydroxide samples are presented in Fig. 3.

It is observed from Fig. 3 that the aluminum hydroxide identified as CAS number 21645-51-2, is basically amorphous. On the other hand, the diffraction pattern of $Al(OH)_3$ with CAS number 1330-44-5 is sharp and well defined. The latter corresponds to the crystalline species termed

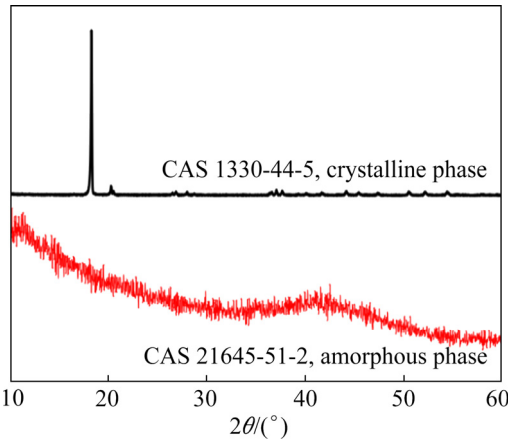

Fig. 3 XRD patterns of aluminum hydroxide samples used in experiments

gibbsite, one of the polymorphic phases of aluminum hydroxide found in nature, which is known as α-$Al(OH)_3$ [36]. With these results, it will be possible to clearly establish if the phase nature is a determining parameter for the precipitation of ettringite from reagents.

3.2 Hydrolyzation and solubility of aluminum hydroxides

Figure 4 presents the Pourbaix diagram of the Al−H_2O system, in which it is observed that hydrolysis of $Al(OH)_3$ producing the aluminate ion (AlO_2^-), the actual reactant that participates in ettringite precipitation, occurs at pH around 11.3; in the case of Al powder, its dissolution occurs according to an electrochemical reaction that generates AlO_2^-, accompanied by the evolution of hydrogen gas, according to the following reaction:

$$Al+H_2O+OH^-\rightarrow AlO_2^-+3/2H_{2(g)} \quad (6)$$

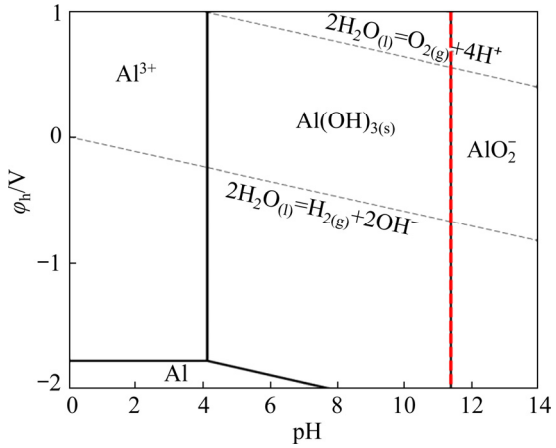

Fig. 4 Pourbaix diagram of Al−H_2O system with 10^{-4} mol/L Al at 25 °C

Figure 5 presents the results of the dissolution kinetics of the aluminum species, and additionally, for comparison, the results obtained with a sample of C70 cement are also presented. It is clearly observed that the amorphous aluminum hydroxide dissolves faster than any of the other species. This result is a clear indicator of the rate at which aluminum ions from amorphous $Al(OH)_3$ pass to the solution, becoming available to the reaction of ettringite, even with a higher rate than that of C70 cement. Interestingly, the crystalline aluminum hydroxide practically does not show any solubility, despite the highly alkaline conditions of the aqueous solution (pH about 12.3), reflecting its low reactivity.

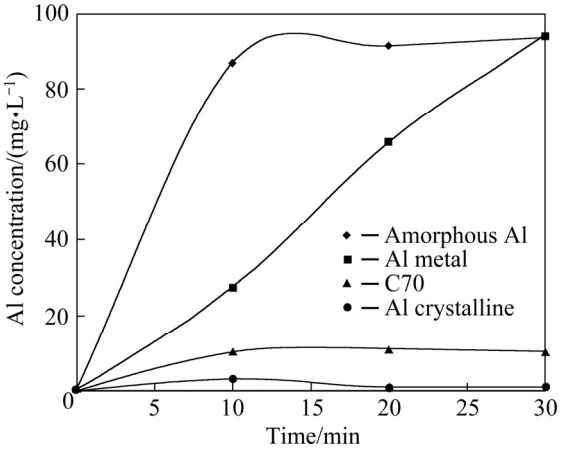

Fig. 5 Dissolution rate of different aluminum sources (1200 g/L CaO and 0.016 mol/L Al)

3.3 Stoichiometry of ettringite precipitation by $Al(OH)_3$

Before continuing with the comparative testing of the crystalline and amorphous aluminum hydroxides, it is important to define the stoichiometric relationship that applies to ettringite precipitation. The Reaction (2) will be used as the basis for the calculations. Furthermore, based on the knowledge that the solution to be treated is a saturated calcium sulfate solution with a concentration of 0.016 mol/L, the stoichiometry of Reaction (2) is expressed as follows:

$$0.016CaSO_4+0.016CaO+0.0106Al(OH)_3+0.15H_2O\rightarrow 5.33\times10^{-3}E \quad (7)$$

where E stands for ettringite.

According to the stoichiometry of Eq. (7), in order to treat 1 L of a saturated calcium sulfate solution (0.016 mol/L), the addition of 896 mg of CaO and 826 mg $Al(OH)_3$ will be necessary, to obtain 6680 mg of ettringite as the solid product.

These additions are calculated considering the exclusive formation of ettringite from aluminum hydroxide, that is, without considering parallel or simultaneous reactions. In addition, to obtain a clearer idea of what happens in the environment of ettringite formation, the HSC Chemistry V 6.1 software was used, with the aim of simulating the studied reaction system in order to calculate the minimum concentration necessary of reactants to precipitate ettringite and other possible solid products, and at the same time, to establish if the resulting concentration of ions in the treated solution gives rise to the lowest ionic strength.

Table 2 shows the results of six simulations, which were obtained as follows: based on the calcium sulfate saturation concentration (0.0168 mol/L) and keeping the CaO addition constant, the $Al(OH)_3$ concentration was cumulatively increased and the resulting equilibrium was computed. The result for the simulation is the one corresponding to the lowest ionic strength of the treated solution. For example, for Simulation 1, the calcium sulfate concentration was 0.0168 mol/L, the CaO addition 900 mg/L and the added $Al(OH)_3$ was varied from 0 to 1200 mg/L; the result with the lowest ionic strength (0.013 mol/L) corresponded to $Al(OH)_3$ addition of 830 mg/L. The above procedure was repeated for all the simulations performed.

According to the data presented in Table 2, additions of 1050 mg/L CaO and 970 mg/L of $Al(OH)_3$ (0.0124 mol/L), give rise to the best conditions of the reaction system, that is, the best compromise between the lowest ionic strength of the aqueous solution and the highest concentration of precipitated ettringite (0.005 mol/L) (see Fig. 6). It is observed from Table 2 and Fig. 6, that the ionic strength and the concentration of ions in the solution, particularly the aluminate ion, increase once the addition of $Al(OH)_3$ exceeds 0.0124 mol/L.

It is worth mentioning that Fig. 6 was obtained considering activity coefficients of ionic species equal to 1, which are the default coefficients set in the HSC software. Therefore, it is necessary to revise the computations of the reaction system to bring it closer to reality. For this, the effect of the ionic strength of the solution on the activity coefficients of the ionic species and, therefore, on their molar concentration will be considered next.

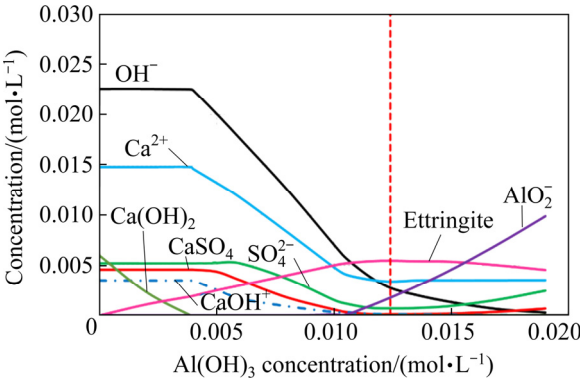

Fig. 6 Species distribution diagram obtained in thermodynamic simulation of reaction between saturated solutions of calcium sulfate (0.0168 mol/L), 1050 mg/L CaO and 0−1200 mg/L $Al(OH)_3$

The optimization of the reaction system, which consisted of the effect of the ionic strength of the solution on the activity coefficient of aqueous species, was performed based on the preliminary results obtained, that is, for the simulation considering the saturated calcium sulfate solution of 0.0168 mol/L, the initial addition of 1050 mg/L CaO and the addition of varying from 0 to 0.019 mol/L with intervals of 0.001 mol/L. The equilibrium concentrations of the ionic species and the ettringite precipitated are plotted against the additions of $Al(OH)_3$ (see Fig. 7). In order to facilitate the interpretation of the behavior of the species in the studied system, Fig. 7 shows that only the ettringite and the ionic species contribute the most to the ionic strength of the aqueous solution.

The dashed line in Fig. 7 shows the locus of the minimum ionic strength of the solution and the largest concentration of precipitated ettringite. By exceeding the optimal addition of $Al(OH)_3$, it is clearly observed that the concentrations of AlO_2^-,

Table 2 Thermodynamic simulation results of $H_2O-CaSO_4-CaO-Al(OH)_3$ system

Simulation No.	Initial concentration*/ (mg·L⁻¹)		Added reactant/ (g·L⁻¹)		Remaining concentration/ (mg·L⁻¹)			Final condition	
	Ca^{2+}	SO_4^{2-}	CaO	$Al(OH)_3$	Ca^{2+}	SO_4^{2-}	Al	pH	I/(mol·L⁻¹)
1	1315	1613	0.9	0.83	161	229	29	11.32	0.013
2	1386	1613	1	0.92	144	123	39	11.49	0.011
3	1422	1613	1.05	0.97	144	81	47	11.56	0.010
4	1458	1613	1.1	1	154	51	55	11.65	0.011
5	1529	1613	1.2	1.01	200	19	57	11.85	0.014
6	1601	1613	1.3	0.99	264	10	45	12.03	0.018

* In the case of Ca^{2+}, the concentration includes the calcium of the $CaSO_4$ saturated solution and calcium added as CaO

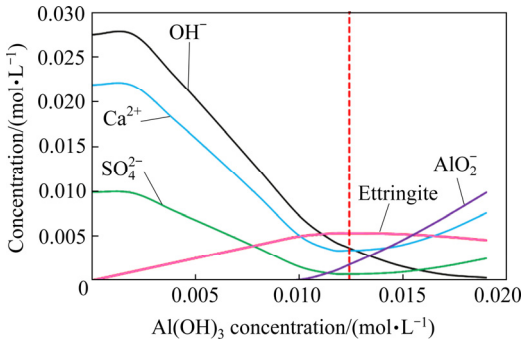

Fig. 7 Optimized species distribution diagram of reaction between saturated calcium sulfate solution with initial addition of 1050 mg/L CaO, and 0−0.019 mol/L $Al(OH)_3$, showing only ionic species present at significant concentrations (The dotted vertical line indicates the condition where the lowest ionic strength occurs)

Ca^{2+} and SO_4^{2-} ions increase, indicating the accumulation of added $Al(OH)_3$ and redissolution of ettringite due to the decrease of pH (decrease of OH^- concentration in Fig. 5) below the pH that defines the stability of ettringite (see Fig. 2).

3.4 Experimental verification of thermodynamic simulation

Figures 8 and 9 show the removal of the calcium as a function of time of the saturated water treated with the two aluminum hydroxide reactants, the amorphous (see Fig. 8) and the crystalline (see Fig. 9). In general, better results are observed with the use of amorphous aluminum hydroxide than those with the crystalline one.

As listed in Table 2, the parameter that determines the completion of ettringite precipitation will be the solution pH of 11.56, according to Simulation 3. Regarding this, in the case of the solution treated with amorphous $Al(OH)_3$ (see Fig. 8), it is observed that the rate of calcium removal appears to be proportional to the calcium concentration itself, until the end of the test at pH 11.56, reached at 150 min. The remaining calcium and sulfate concentrations were 130 and 175 mg/L, respectively. Comparing these values with the thermodynamic simulation, the calcium concentration experimentally obtained is slightly lower (144 mg/L, see Table 2); however, the remaining sulfate concentration is much higher than the predicted one (81 mg/L). It is worth mentioning that additional tests were carried out with a slight excess of reactants, without observing significant changes in the concentrations of calcium and sulfate obtained.

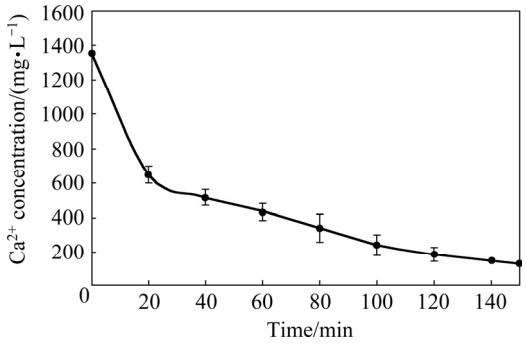

Fig. 8 Evolution of calcium removal as function of time (0.016 mol/L calcium sulfate solution treated with 1050 mg/L CaO and 970 mg/L of amorphous $Al(OH)_3$)

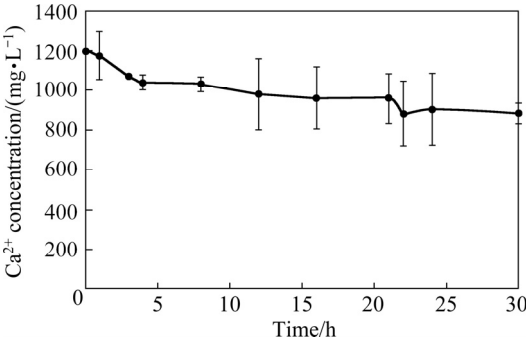

Fig. 9 Evolution of calcium removal as function of time (0.016 mol/L calcium sulfate solution treated with 1050 mg/L CaO and 970 mg/L crystalline $Al(OH)_3$)

Despite the relative discrepancy between the results of the thermodynamic simulation and the experimental data obtained with the amorphous aluminum hydroxide, the measured calcium and sulfate concentrations fall within the limits fixed for drinking water by international standards [37]; furthermore, such concentration, does not significantly affect the flotation performance of the economic interest sulfide species, such as galena [5].

Regarding the use of crystalline $Al(OH)_3$, its low reactivity is evident as shown in Fig. 9, even though the test lasted for around 30 h. Furthermore, when the remaining sulfate concentration was analyzed (around 1500 mg/L), it was observed that this was practically the same as the initial concentration, confirming that the formation of ettringite did not occur. Finally, the calcium concentration slightly decreased due to the formation of calcite ($CaCO_3$), since under alkaline pH the precipitation of calcite is inevitable due to

the absorption of the atmospheric carbon dioxide, which produces carbonate ions under alkaline conditions. In relation to this latter issue, the filtered solids of both tests were characterized by XRD (Figs. 10 and 11).

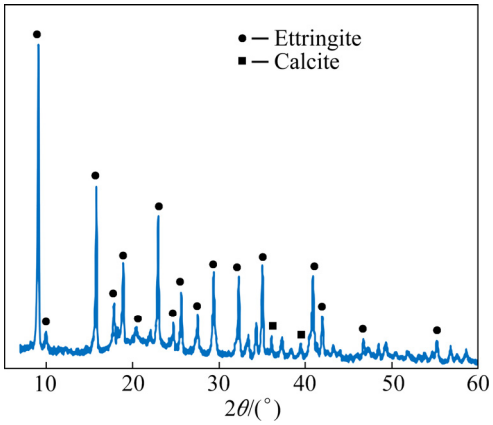

Fig. 10 XRD pattern of solids produced by 0.016 mol/L saturated solution of $CaSO_4$, with 1050 mg/L CaO and 970 mg/L of amorphous $Al(OH)_3$

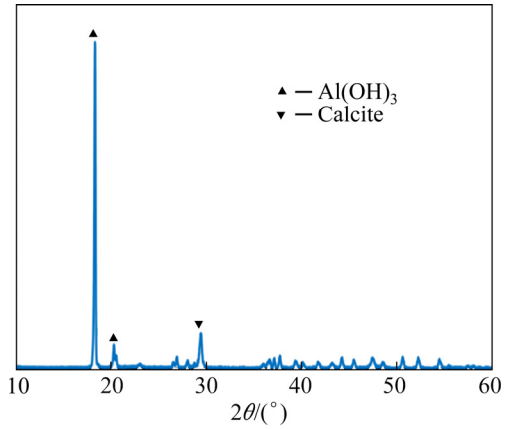

Fig. 11 XRD pattern of solids produced by saturated solution of 0.016 mol/L $CaSO_4$, with 1050 mg/L CaO and 970 mg/L of crystalline $Al(OH)_3$

Figure 10 shows the evident formation of ettringite when amorphous aluminum hydroxide was used to treat the calcium sulfate solution. Likewise, it is observed that some calcium was consumed by the carbonate ion present in the solution due to the absorption of atmospheric CO_2, which causes the precipitation of calcite. This behavior may be due to the occurrence of parallel reactions to the precipitation of ettringite, which consumes calcium instead of sulfate, thus reducing the driving force for ettringite precipitation (i.e., sulfate consumption). On the contrary, it is observed from Fig. 11 that ettringite did not precipitate when crystalline aluminum hydroxide was used, so the calcium concentration decreased during the test due to the precipitation of calcite since this species is also present in the solid product.

The low reactivity of gibbsite ($Al(OH)_3$) can be attributed to its crystalline nature since its atomic arrangement is composed of OH^- ions layers, which are intercalated with Al^{3+} ions layers in a compact packaging. The attractive forces between the hydroxyl and aluminum ions, in addition to the repulsive forces between the Al^{3+} ions which are distributed in hexagonal rings between the OH^- ions [38], allow the arrangement of ions to be at equilibrium. This structure allows a large part of the surface of the OH^- ions to be linked between the aluminum ions, causing surface to be unavailable to react with other ions of the solution. This arrangement limits the reactivity of OH^-, thereby causing the reactivity of Al^{3+} ions contained between the hydroxyl ions to be even more restricted to react with neighboring ions. The compact packaging and the force between the bonds of the crystalline $Al(OH)_3$ structure, lead to inactivity in the studied reaction system, giving rise to the inert behavior observed regarding the precipitation of ettringite from reactant in alkaline medium.

On the contrary, the disordered atomic arrangement of amorphous aluminum hydroxide of lower binding forces between the ions, compared to the force involved in ionic bonds of crystalline aluminum hydroxide, allows the amorphous hydroxide to participate in reactions of lower activation energy and faster kinetics [39]. The unarranged structure itself, of greater specific surface area, prevents compact packaging of the Al^{3+} and OH^- ions, thus being more available to react and interact with the ions of the aqueous solution. This physical−chemical characteristic of amorphous aluminum hydroxide allows the solid to be more reactive, compared to the crystalline equivalent.

3.5 Removal kinetics of calcium and sulfate ions with amorphous aluminum hydroxide at different temperatures

Ettringite precipitation essentially depends on the concentrations of Ca^{2+}, SO_4^{2-} and OH^- ions, as shown in Reaction (3). As illustrated in Fig. 2, the

pH of the solution must be kept within the narrow range between 11.5 and 12, in order to assure the stability of ettringite [38]; according to this, it may be assumed that the concentration of OH^- ions remains approximately constant during the precipitation reaction and therefore, the rate of ettringite precipitation (directly proportional to the rate of calcium removal) will depend solely on the concentrations of Ca^{2+} and SO_4^{2-} ions, according to the following equation:

$$-\frac{d[Ca^{2+}]}{dt}=k[Ca^{2+}][SO_4^{2-}] \quad (8)$$

where k is the rate constant.

According to Eq. (1), the concentration of sulfate may be expressed in terms of calcium concentrate as follows:

$$[SO_4^{2-}]=\frac{[Ca^{2+}]}{2} \quad (9)$$

Combining Eqs. (8) and (9) and making $k'=k/2$, Eq. (10) is obtained,

$$-\frac{d[Ca^{2+}]}{dt}=k'[Ca^{2+}]^2 \quad (10)$$

which may be integrated from the initial calcium concentration $[Ca^{2+}]_o$ at time $t=0$, to a concentration of $[Ca^{2+}]$ at time t:

$$[Ca^{2+}]=\frac{[Ca^{2+}]_o}{1+[Ca^{2+}]_o k't} \quad (11)$$

According to Eq. (11), the rate of ettringite precipitation will be reflected by the evolution of calcium concentration in solution.

In order to evaluate the effect of temperature on the rate of calcium consumption (e.g., ettringite precipitation), a series of experiments were carried out, making use of the optimal conditions dictated by the thermodynamic simulation. The temperature was varied between 15 and 35 °C, with intervals of 5 °C, considering that this is the range in which the process water temperature varies in most of the sulfide flotation operations around the world, due to seasonal variations.

Figure 12 shows the evolution of calcium concentration as a function of time, at the different temperatures. The results clearly show that calcium removal rate increases as the temperature increases.

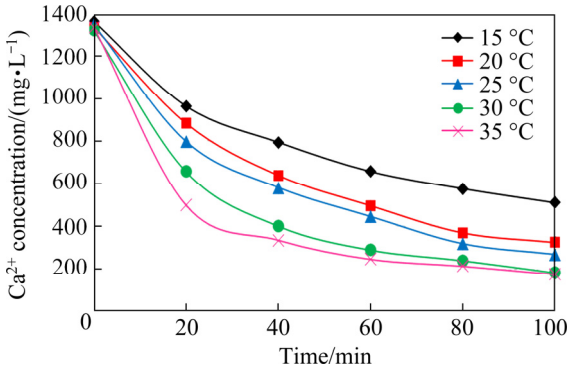

Fig. 12 Evolution of calcium concentration as function of time at different temperatures (0.016 mol/L saturated solution of $CaSO_4$, 1050 mg/L CaO and 970 mg/L of amorphous $Al(OH)_3$)

If Eq. (11) correctly describes the observed experimental behavior, the apparent rate constant for each of the experiments carried out was estimated, which will obtain an estimate of the activation energy of the ettringite precipitation under the tested conditions. Table 3 presents the estimated values of the apparent rate constant k' at the different temperatures, as well as the calcium concentrations at the beginning and end of the test. The rate constants were estimated by minimizing the sum of the squares of the differences between the experimentally measured calcium concentration and those estimated by Eq. (11).

It is observed in Table 3 that the final calcium concentration decreases as the temperature of the test is increased, contrary to the behavior of the rate constant, which increases as the temperature of the reaction system increases.

Table 3 Rate constants as function of temperature, and initial and final calcium concentrations

Experimental temperature/°C	Initial Ca^{2+} concentration/(mg·L^{-1})	Final Ca^{2+} concentration/(mg·L^{-1})	Rate constant, k'/(10^{-5} L·mol^{-1}·s^{-1})	R^2
15	1365	511	1.31	0.98
20	1338	324	2.14	0.96
25	1348	268	2.63	0.98
30	1325	182	4.21	0.83
35	1338	174	5.71	0.81

Once the rate constant was estimated for each of the tested temperatures, the activation energy was calculated by means of the Arrhenius equation, assuming k may be approximated by the estimated apparent rate constant (k'):

$$k = A\exp[-E_a/(RT)] \quad (12)$$

where A is the frequency factor, E_a is the activation energy of the reaction (J/mol), R is the gas molar constant, and T is the thermodynamic temperature.

By plotting Eq. (12) as ln k vs $1/T$ (see Fig. 13), the activation energy can be estimated from the slope of the straight line (slope=$-E_a/R$).

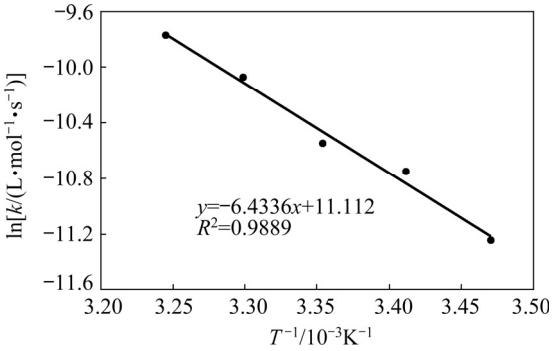

Fig. 13 Arrhenius plot presenting ln k vs $1/T$, and equation of straight line obtained

Based on the results shown in Fig. 13, the estimated value of the slope is -6.4336×10^3 K, from which a value of 53.48 kJ/mol is obtained for E_a. In this regard, the activation energy values determine whether the reaction is controlled by diffusion or by chemical reaction. According to HABASHI [40], when the reaction is controlled by diffusion, the activation energy values are generally below 5 kJ/mol, while activation energy values greater than 40 kJ/mol correspond to processes controlled by the chemical reaction [41]. According to the above analysis and based on the value of the activation energy obtained, it can be concluded that the ettringite precipitation process is controlled by the chemical reaction.

In order to determine if the estimated rate constant values (Table 3) adequately predict the ettringite precipitation reaction, and therefore the decrease in calcium in solution, the calcium in concentration expressed by Eq. (8) was estimated making use of the k' for each tested temperature. The estimates obtained from the modeling, as well as the experimentally measured concentration, are presented in Fig. 14. The excellent fit that exists between the kinetic model and the experimental data, corroborates that the ettringite precipitation reaction from a saturated calcium sulfate solution treated with amorphous $Al(OH)_3$, appears to correspond to a second order reaction, and this may be expressed as a function of the calcium concentration. This finding also corroborates the chemical reaction expressed by Eq. (2), which is suggested to occur between the calcium sulfate solution and the aluminum hydroxide.

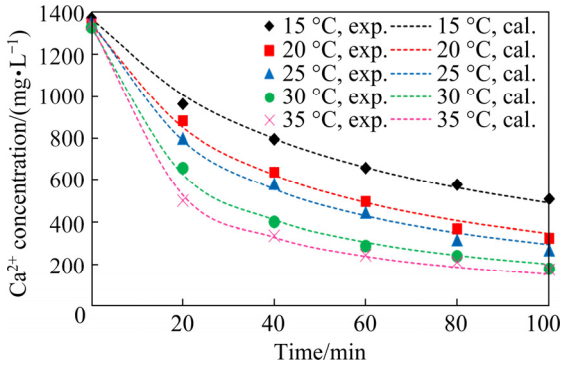

Fig. 14 Calcium ion concentration as function of time at different temperatures (a saturated solution of 0.016 mol/L $CaSO_4$, with 1050 mg/L CaO and 970 mg/L of amorphous $Al(OH)_3$)

4 Conclusions

(1) Calcium and sulfate in saturated solutions of gypsum were removed in the form of ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$) with the addition of 1050 mg/L CaO and 970 mg/L of amorphous $Al(OH)_3$. Removals of 83% calcium and 91% sulfate were achieved with a reaction time of 150 min.

(2) Ettringite precipitation appeared to be described by a second-order reaction. The suggested kinetic model showed a good fit between the predictions and the calcium concentration experimentally measured.

(3) The removal process was apparently governed by chemical reaction, as suggested by the activation energy of the system 53.48 kJ/mol.

(4) It was found that temperature plays a significant role in ettringite precipitation, since the removal of calcium increased from 32% to 77% by increasing temperature from 15 to 35 °C.

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用氢氧化铝处理浮选循环水同时脱除钙离子和硫酸根离子

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摘　要：由于环境政策和经济因素，复杂硫化物矿的一些浮选作业用水循环使用，导致某些离子的浓度逐渐升高，影响到相关矿物的浮选。在此背景下，对含有高浓度钙和硫酸盐离子的合成溶液的处理进行实验研究和热力学分析。重点评估两种铝化合物对于 Ca^{2+}和 SO_4^{2-}以钙矾石形式析出过程的作用。结果发现，非晶态氢氧化铝比晶态氢氧化铝更为有效，可脱除高达 83%的钙和 91%的硫酸盐。对所得固体样品的 XRD 分析表明，因为吸收了大气中的二氧化碳, 主要反应产物为钙矾石，伴随着少量的方解石。化学处理后的最终溶液中残留钙和硫酸盐的浓度低于 200 mg/L。动力学研究发现，钙脱除过程对于钙浓度为二级反应，表观活化能为 53.48 kJ/mol，表明钙矾石析出过程可能受化学反应控制。

关键词：钙矾石；离子去除；氢氧化铝；钙；硫酸盐

(Edited by Xiang-qun LI)