



Sulphate ions removal from an aqueous solution: I. Co-precipitation with hydrolysed aluminum-bearing salts

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ABSTRACT

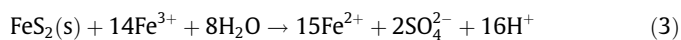
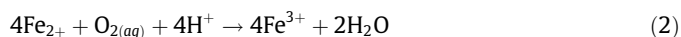
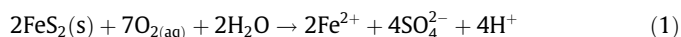
The removal of sulphate ions constitutes one of the main challenges in the mining, metallurgical and chemical industries, among others. Sulphate removal from aqueous streams is by far one of the most difficult and onerous tasks in these industries, and most existing processes are inefficient and costly. This work presents a method to remove sulphate ions in an acidic medium based on co-precipitation with aluminum salts, namely AlCl_3 and a polyaluminum salt (PAC), followed by filtration. Herein, the different Al species react differently with sulphate, forming soluble and insoluble complexes, the latter of which causes insolubility and allows for the removal. The reaction kinetics depend on the activity of the so-called Al_b species (which are classified as polymeric) and was proved here by different techniques. Better results were obtained with the inorganic salt AlCl_3 , when compared to PAC, probably because of the higher activity of the Al species. Co-precipitation of sulphate depends highly on the pH (which is optimal at 4.5), the mass ratio between reagents and sulphate ions (which is optimal at 7:1) and time (10 min). Finally, it was concluded that the technique proposed here has good potential for the treatment of sulphate-bearing effluents, including acid mining drainage (AMD).

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1. Introduction

Sulphate ions are naturally present in several mineral and metallurgical wastewaters after processing Barite (BaSO_4), Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and metal sulphides (mainly Fe, Cu and Mo) (Greenwood and Earnshaw, 1997). High levels of sulphate ions cause severe environmental problems, especially in the mining, metallurgical, chemical and agricultural sectors. Tailings (piles or dumps) from coal and some metal-bearing ores (especially those rich in pyrite and chalcopyrite) are readily oxidised by water and oxygen, resulting in acid drainage. Such liquid effluents or AMDs (acid mine drainages) contain high levels of heavy metal ions, sulphate ions and acidity and constitute one of the main challenges in the mining industry.

The reactions involving the oxidation of pyrite are expressed as follows (Kontopoulos et al., 1995; Kontopoulos, 1998):



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If the oxidation potential is maintained, the proton acidity produced (Eq. (1)) may be consumed in the oxidation of Fe^{2+} to Fe^{3+} by the oxygen (Eq. (2)). Further, the Fe^{3+} generated by the reaction will oxidise FeS_2 by the indirect reaction (Eq. (3)), generating more sulphate ions. The resulting Fe^{2+} will be oxidised to Fe^{3+} again (Eq. (2)) and will be available to oxidise more pyrite (autocatalysis) (Kontopoulos, 1998).

AMD eventually migrates into superficial and subterranean waters, small streams and rivers, creating severe problems in coal- and ore-producing countries (Kontopoulos, 1998; Rubio et al., 2007), one of which is the removal of sulphate ions.

Other industrial activities involve handling sulphate ion-bearing effluents found in the production of fertilisers, dyes, glass, paper, soaps, textiles, fungicides, leather and metals.

Sulphate can cause various kinds of problems depending on its concentration and on the earth alkaline cation (Morris and Levy, 1983). Common examples include an altered taste of water, digestion troubles in animals and humans, soil acidification and corrosion of metals.

Sulphate ions are some of the main contributors to so-called water "mineralisation", thereby increasing the conductivity and corrosion potential of receptor bodies. These anions promote the following, among other things: corrosion and scaling in pipes, structures and equipment; fouling and deposition in boilers; and acidification of soils and blockage of soil pores, retarding irrigation

or water drainage (Bowell, 2000). Table 1 summarises some of these problems.

The World Health Organisation (WHO) has established the maximum tolerable level of sulphate in water as 500 mg L^{-1} , but many countries have recommended lower values, such as the 250 mg L^{-1} recommended by Brazil and the USA (Ministry of Health in Brazil, 2004; US EPA, 1991).

The removal of sulphate ions from such waters is a complex problem due to the high solubility and stability of these anions in aqueous solutions. Partial sulphate ions removal is often accomplished through precipitation with lime (Rubio et al., 2009). However, this process usually presents a very low practical efficiency because of the high solubility of the produced CaSO_4 .

The main processes for treating sulphate ion-bearing water are as follows: (1) biological degradation (Maree and Strydom, 1985; Maree and Strydom, 1987); (2) membrane filtration (mainly reverse osmosis) (INAP, 2003); (3) adsorption and/or ion exchange (Lopez, 2009); and (4) chemical precipitation. The main characteristics (advantages and disadvantages) observed for each process are summarised in Table 2.

Many researchers have studied the coagulation performance of PACs, even for sulphate ion removal (Parker and Bertsch, 1992; Tang et al., 2002; Gao et al., 2006). It has been found that the coagulation performance of PACs is closely related to the Al species distribution, the basicity (B) and the Al_T concentration. Recent studies carried out by Zhao et al. (2009) have shown that the PAC produced by Ca-based basification reagents has advantages over that generated using NaOH as the basification reagent because Ca reagents have a low solubility in water and are ideal for reducing the production and release of OH^- . Additionally, the produced Ca^{2+} compresses the electric double layer of the colloid particles, which may improve the flocculation performance to some extent.

Fig. 1 shows a schematic distribution of aluminum species and their interactions with sulphate ions in solution. The content of the three species can be calculated according to the known total concentration of aluminum (Al_T):

$$\text{Al}_T = \text{Al}_a + \text{Al}_b + \text{Al}_c \quad (4)$$

Parker and Bertsch (1992), Tang et al. (2002) and Gao et al. (2006) show that the soluble species (generating soluble complexes with sulphate ions) designated as Al_a is assumed to include primarily monomeric species. Al_b is thought to include polynuclear Al species and to possess structures that are fairly stable and withstand further hydrolysis, resulting in higher coagulation efficien-

cies. The fraction of aluminum that precipitates as hydroxide salts is assumed to represent the colloidal or solid phase (Al_c) (Gao et al., 2006).

This work is part of a series of articles aimed at enhancing and provoking discussion on the removal of sulphate ions by physico-chemical mechanisms. This first study evaluates the co-precipitation of sulphate ions onto aluminum colloids. The results are explained by the thermodynamic solution equilibrium and the electrostatic attractions between the sulphate ions and aluminum species.

2. Material and methods

2.1. Materials

Sodium sulphate anhydrous (P.A.) was employed in the preparation of sulphate solutions. Polyaluminum chloride (Panfloc® TE1018 – Pan-Americana S.A.) and aluminum chloride (AlCl_3 – VETEC®) were used as aluminum sources (reagents) in the sulphate ion co-precipitation. HCl (Quimex®) and NaOH (Vetec®) were utilised for pH adjustment. Cellulosic membranes ($0.45\text{-}\mu\text{m}$ pore diameters) were used as disc filters. All solutions were prepared using deionised water, and the results were obtained in duplicate tests.

2.2. Methods

2.2.1. Co-precipitation with aluminum salts

The pH of the solution was determined using the pH meter ANALION® (Model AM 608), and bench-scale precipitation experiments were conducted in beakers (250 mL) under magnetic stirring. Sulphate ion concentrations were measured by ionic chromatography (861 advanced compact IC – Metrhom®), and the results were expressed as $\text{mg SO}_4^{2-} \text{ L}^{-1}$. SEM/EDS photomicrographs of precipitates were taken using a Jeol (JSM-6060 model) microscope.

2.2.2. Effect of pH

Sulphate co-precipitation with PAC TE1018 and AlCl_3 was carried out over several pH values ranging from 3 to 10.5. Five-hundred-millilitre volumes of 700, 1000 and 1800 mg L^{-1} sulphate solutions were conditioned with aluminum reagents for 30 s at 15 rpm stirring. The reagent: SO_4^{2-} ratio was kept at 7:1 (related to [PAC] and [AlCl_3]), and colloidal precipitates were filtered after 10 min for subsequent sulphate determination.

Table 1

Effect of different sulphate ions concentrations on health and industrial problems.

Sulphate concentration (mg L^{-1})	Comments	References
237, 370 and 419 (sodium, calcium and magnesium salts, respectively)	Sulphate concentration changing the taste of water	Whipple (1907), cited by WHO (2004)
1000 and 850 (calcium and magnesium salts, respectively)		Zoeteman (1980)
* 8–7 g	*Mass and concentration of sulphate enough to cause diarrhoea in humans	Cocchetto and Levy (1981) and Morris and Levy (1983)
600		US DHEW (1962), Chien et al. (1968), cited in WHO (2004)
1200		US EPA (1999)
630–1150		Chien et al. (1968)
1000		WHO (2004)
600		Esteban et al. (1997)
–	Corrosion in concrete components and aluminum plates	Kolics et al. (1998)
25,000		Dehwah et al. (2002)
3200	Formation of CaSO_4 deposits in plate heat exchangers. Fouling potential increased onto membrane surface	Bansal et al. (2000)
780		Singh and Song (2006)

* Values given according total mass of sulphate ions, independently of the water volume.

Table 2
Main sulphate ions removal processes: advantages and disadvantages.

Process	Advantages	Disadvantages
<i>Biological reduction</i> Anaerobic systems	Low costs Easy to operate	Long residence time Organic material residuals Large area
<i>Membrane filtration</i> Reverse Osmosis and ultrafiltration	High efficiency Short time	High costs Large wastewater volume
<i>Adsorption and/or ion exchange</i> Sulf-IX™ (Lopez, 2009) Alternative sorbents (chitosan) (Moret and Rubio, 2003)	High efficiency Sulphate levels lower than 250 mg L ⁻¹ Costs are lower than reverse osmosis processes	Requires frequent bed regeneration Handling difficulties of chitosan Tailing generated in the regeneration of resins
<i>Chemical precipitation</i> Barium sulphate precipitation (Kun, 1972; Trusler et al., 1988 and Solari, 2006) Crystallisation of sulphate salts by evaporation (El Teniente-CODELCO-Chile, pilot study treating 2–4 m ³ s ⁻¹) Ettringite precipitation (3CaO·3CaSO ₄ ·Al ₂ O ₃ ·31H ₂ O) at pH 12 (Cadorin, 2007)	Short time High kinetics Low solubility independent of pH High efficiency	High costs Large sludge generation Residual concentration of barium

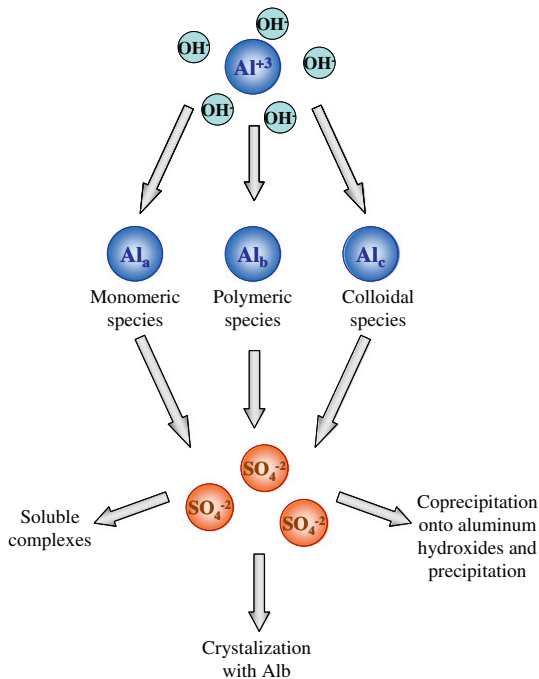


Fig. 1. Aluminum species distribution and interaction with sulphate ions in solution (model adapted from Xu et al. (2004)).

2.2.3. Effect of reaction time, PAC/SO₄²⁻ ratio and ionic strength

The kinetics of the reactions were studied by monitoring the sulphate removal with time. Then, the effect of the PAC/SO₄²⁻ ratio on the co-precipitation of the anion was investigated by varying the ratio between 3:1 and 26.4:1 in solutions containing 700, 1000 and 1800 mg L⁻¹ of sulphate. Next, 100 mL of those solutions were conditioned for 10 min before filtration and sulphate analysis. The effect of the ionic strength on the co-precipitation reactions was evaluated using four different NaNO₃ solutions (0.05, 0.1, 0.2 and 0.5 Mol L⁻¹ of NO₃⁻).

2.2.4. DAF and lamella settling tests

Laboratory and pilot studies were carried out using dissolved air flotation at the bench and lamella settling in continuous studies. In the beginning, PAC and AlCl₃ were conditioned for 1:1, 3:1 and 5:1

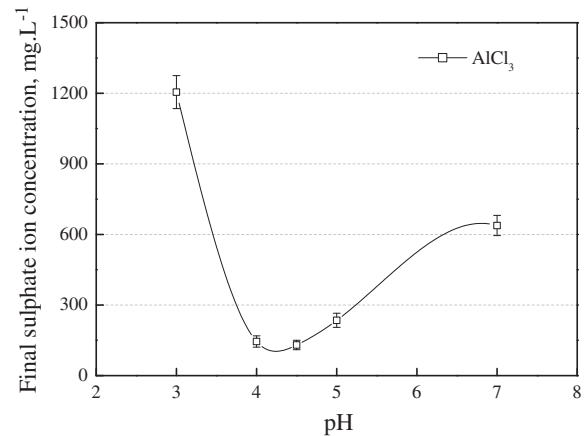


Fig. 2. Effect of pH on sulphate ion co-precipitation onto aluminum colloids precipitates. reagent:sulphate ratio = 7:1. Initial sulphate ions: 1800 mg L⁻¹. Conditioning time: 10 min.

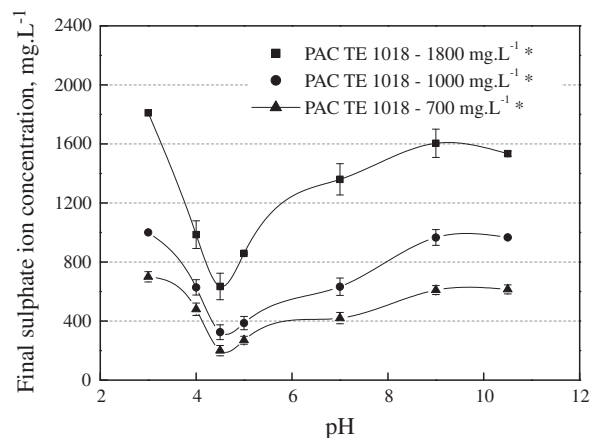


Fig. 3. Effect of pH on sulphate co-precipitation with polyaluminum chloride. PAC:sulphate ratio = 7:1. Conditioning time: 10 min. * = Initial sulphate ion concentration.

reagent:SO₄²⁻ ratios. After, the pH was adjusted to 4.5, and flocculation was performed with 30 ppm of cationic polyacrylamide (Nalco 8589). Dissolved air flotation (DAF) experiments were carried out at the bench with a 4 kgf cm⁻² saturation pressure, 30% recycle flow (saturated water) and 20 mg L⁻¹ oleate of sodium in the floc collection stage. A pilot study of lamella settling (LS) used in recent experiments for metal ion removal from acid mine drainage in south Brazil (NF-LS process; see details in Rubio et al., 2009) was performed at a 1 m³ h⁻¹ flow rate with special hydraulic devices for flocculation, namely, the Flocs Generator Reactor (FGR) and Serpentine Flocculator (Rubio et al., 2009).

3. Results and discussion

3.1. Effect of pH

Figs. 2 and 3 show the effect of pH on sulphate ions using aluminum-bearing reagents. A pH of 4.5 appeared to be the ideal condition for sulphate adsorption on aluminum precipitates (or co-precipitation).

The best results for sulphate ion removal were found using AlCl₃ reagents at pH 4.5 (>85%) for an initial sulphate ion concentration of 1800 mg L⁻¹.

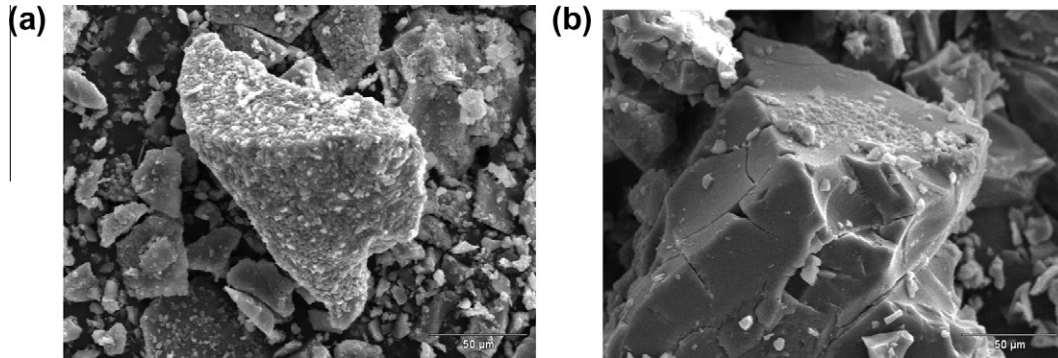


Fig. 4. (a) SEM Photomicrographs of sulphate ions deposition onto PAC precipitates. (b) SEM Photomicrographs of PAC precipitates in deionised water. Bar length is 50 µm and the magnification 550×. pH 4.5 and 1800 mg L⁻¹ initial sulphate ions concentration.

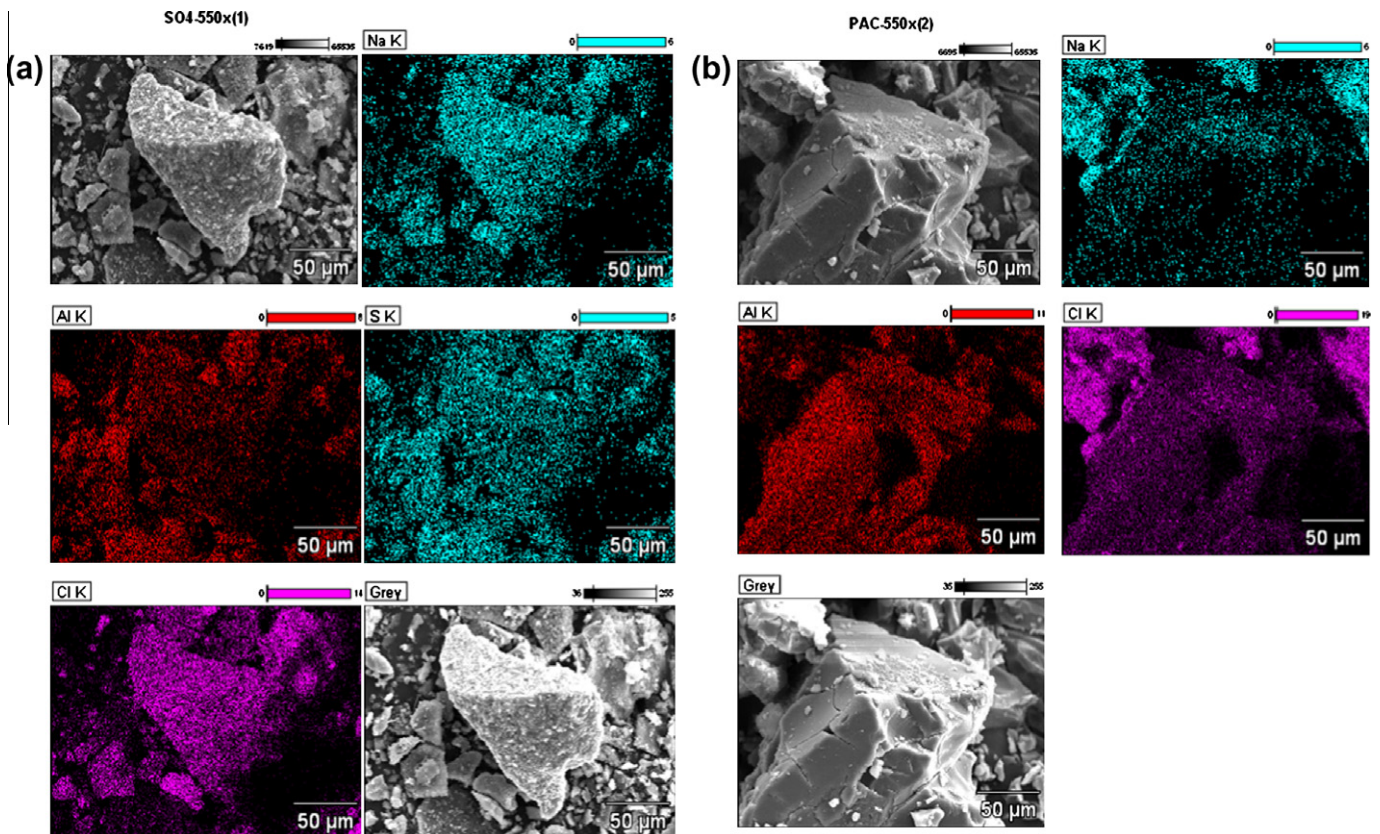


Fig. 5. (a) EDX analysis showing elements distribution in PAC-sulphate precipitates at pH 4.5. (b) EDX analysis showing elements distribution in PAC precipitates without sulphate ions in solution at pH 4.5. Bar lengths are 50 µm and the magnification is 550×.

Similar to our present work, Xu et al. (2004) found a pH range of 4.5 to 5.0 to be the best condition in which Al_b species predominate and interact with sulphate ions. Cadornin (2007) showed the importance of Al_b species in PAC kinetics reactions with sulphate ions and that Al_a species react with sulphate to form a soluble complex. Moreover, Tang et al. (2002) studied the effect of sulphate ions on the coagulation of kaolinite using polyaluminum chloride. They explained that the high concentration of anions in solution can contribute to aluminum salt coagulation by the neutralisation of positive electrostatic charges. The authors also demonstrated that sulphate ions interact with polymeric aluminum species (Al_b), accelerating the kinetics of coagulation.

Aluminum salts do not precipitate at pH levels below three because of the solubility of aluminum hydroxides in acidic mediums. This fact prevents sulphate ion removal by co-precipitation mechanisms.

Fig. 4a shows small sulphate-bearing spots deposited on the outer surface of polyaluminum chloride precipitates (PACs), and Fig. 4b shows PACs in the absence of sulphate ions. These results can be explained by the Energy Dispersive X-ray (EDX) analysis, which provided a comprehensive interpretation of the elements in the overall interaction.

In Fig. 5a, aluminum and sulphate associations are distributed throughout all images, whereas sodium and chlorine elements are associated as bigger salt grains. Also, sulphur (sulphate) elements could not be identified by EDX analysis when PAC precipitates were not submitted to sulphate ion adsorption (Fig. 5b). This technique demonstrates the strong electrostatic interaction between Al, mainly Al polymeric species ($Al_{13} - AlO_4Al_{12}(OH)_{24}(-H_2O)_7^{+12}$), and SO_4^{2-} elements at a pH of 4.5.

3.2. Effects of kinetics and mass ratio

Fig. 6 shows that the reactions for both Al-bearing salts proceed rapidly, with the equilibrium time of sulphate ion co-precipitation onto aluminum colloids attained after 10 min of conditioning. Better results were obtained with $AlCl_3$ as compared to PAC; for $AlCl_3$, final concentrations of about 250 ppm were readily obtained for an initial sulphate dosage of around 1800 ppm.

As the reagent concentration increased, the sulphate ions removal also increased, probably due to the higher volume and surface area of the colloidal precipitates; the anions appeared to be deposited and adsorbed electrostatically.

Figs. 6 and 7 show a very low final sulphate concentration at the 7:1 mass ratio, between $AlCl_3$ and sulphate ($mg\ mg^{-1}$), and a high efficiency at pH 4.5. The final sulphate ion concentration was $<250\ mg\ L^{-1}$, which is the drinking water standard limit in Brazil (down from an initial concentration of $1800\ mg\ L^{-1}$). The World Health Organisation's recommendation for the emission limit ($500\ mg\ L^{-1}$) was attained using a 5:1 mass ratio. However, residual aluminum ion contents were present in concentrations of about 181, 220, 265 and $306\ mg\ L^{-1}$ for 3:1, 5:1, 7:1 and 10:1 PAC: SO_4^{2-} ratios, respectively. Therefore, the removal of sulphate ions, at least that by co-precipitation onto colloids of aluminum at pH 4.5, appears to require an optimisation of the PAC: SO_4^{2-} ratio by the use of another Al source or mixtures with iron salts, for which efforts are underway in our laboratory.

Fig. 8 shows sulphate removal as a function of the PAC: SO_4^{2-} ratio at pH 4.5 for three initial SO_4^{2-} dosages. A final sulphate ion concentration of $500\ mg\ L^{-1}$ (WHO recommendation) was attained only at the 8:1 mass ratio between PAC:sulphate, for an initial sulphate ion concentration of $1800\ mg\ L^{-1}$, the latter being the minimum concentration obtained by the conventional process using lime for gypsum precipitation (Silva, 2009).

Table 3 shows the effect of the $NaNO_3$ concentration on sulphate ion removal at pH 4.5. The results show a decrease in the re-

moval process efficiency with a slight, but significant, increase in the residual sulphate ion concentration when the $NaNO_3$ is concentration increased. This is very important when dealing with highly

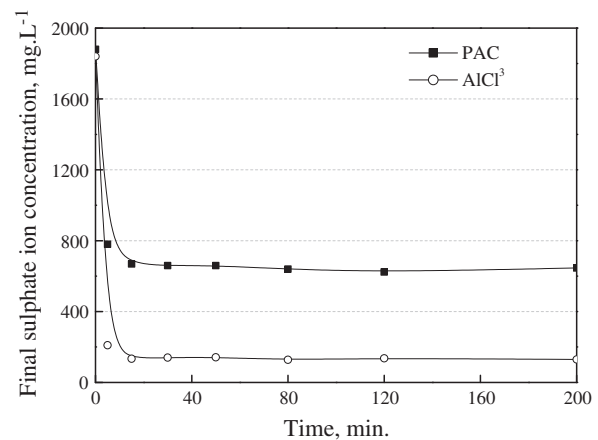


Fig. 6. Kinetics of sulphate ions removal with PAC and $AlCl_3$, at pH 4.5. Coagulant:sulphate ratio 7:1. Initial sulphate ions concentration: $1800\ mg\ L^{-1}$.

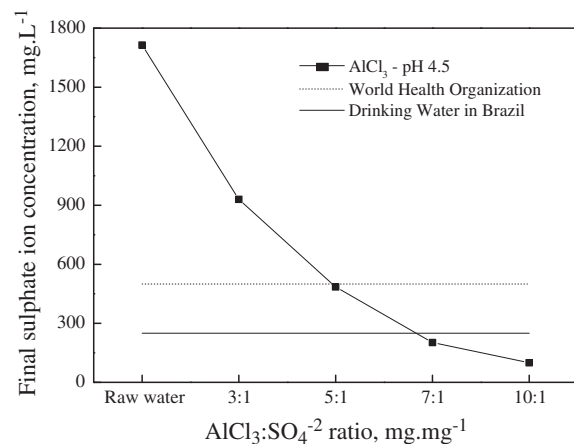


Fig. 7. Effect of $AlCl_3:SO_4^{2-}$ ratio in co-precipitation of sulphate ions onto colloids. pH 4.5. Conditioning time: 10 min. Initial sulphate ions concentration: $1800\ mg\ L^{-1}$.

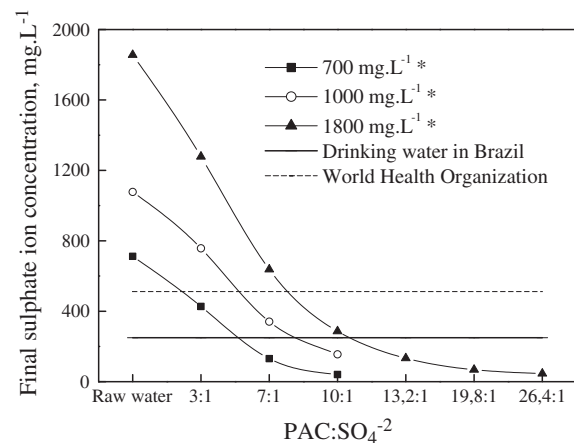


Fig. 8. Effect of PAC: SO_4^{2-} ratio in sulphate ion removal, measured by the final (residual) sulphate concentrations. pH 4.5. Conditioning time: 10 min. * = Initial sulphate ions concentration.

Table 3

Effect of ionic strength on removal of sulphate ions using Al-bearing salts, at pH 4.5. Conditioning time: 10 min. Initial sulphate ion concentration = 1800 mg L⁻¹. Cf = Final sulphate ion concentration (residual, after co-precipitation).

NaNO ₃ (M)	PAC C _f (mg) SO ₄ ²⁻ (L ⁻¹)	AlCl ₃ C _f (mg) SO ₄ ²⁻ (L ⁻¹)	Removal of SO ₄ ²⁻ with PAC, %	Removal of SO ₄ ²⁻ with AlCl ₃ , %
0	675	136	62	92
0.05	677	126	62	93
0.1	673	140	63	92
0.2	733	220	59	88
0.5	822	216	54	88
1	870	245	52	86
5	920	263	49	85

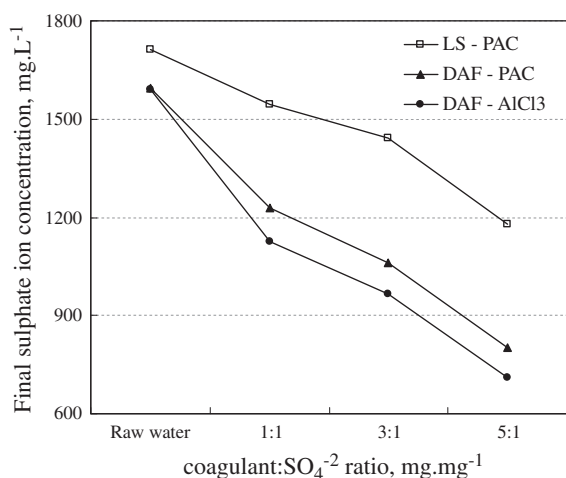


Fig. 9. Comparative solid/liquid separation of flocs by Dissolved Air Flotation and Lamella Settling (LS): Applications for acid mine drainage treatment including sulphate removal at pH 4.5. DAF results obtained at lab scale and LS data from pilot scale experiments.

concentrated effluents such as AMD. It is believed that these results may be due to an effect of the ionic strength on the formation and configuration of PAC precipitates, thereby decreasing the sulphate removal.

Applications of these techniques for sulphate removal are currently underway in laboratory and pilot studies. Preliminary results were obtained from a pilot plant installed in an acid mine drainage (pH < 3) site in South Brazil (Capão da Roça). Herein, coal tailings, which are rich in metal sulphides, were disposed of for years, and the generated AMD (a volume of 90,000 m³) is now treated by neutralisation–flocculation and settling in basins. However, no removal of sulphate ions has been possible.

This work involved separation of the flocculated colloidal precipitate by DAF at a lab scale and by lamellar settling at the pilot plant, with both processes substituting the filtration stage already discussed. Flocculation was performed with 30 ppm of cationic polyacrilamide (Nalco 8589) using a hydraulic device flocculator (RGF; see Rubio et al., 2009). The results are shown in Fig. 9.

DAF appear to be more effective than lamellar settling, probably because of some difficulties in the kinetics of settling of the rather loose and light flocs. Such comparative studies must continue at the pilot plant to elucidate these findings.

4. Conclusions

Sulphate ions (sodium salts) were co-precipitated and were removed from water with aluminum-bearing colloids, formed from

the hydrolysis of either AlCl₃ or polyaluminum chloride (PAC) and reacted under different conditions of solution pH, time and reagent/sulphate ratio. The best results were obtained with AlCl₃ at a pH of 4.5 (>80% sulphate ions removal), a 10 min. reaction time and a 7:1 AlCl₃/SO₄²⁻ ratio. The results with PAC showed a lower efficiency, at around 64% for a 10:1 mass ratio. The formation of aluminum polymer species (Al_b) appears to be responsible for the mechanisms involved in sulphate removal, thus confirming earlier results. Pilot plant and laboratory studies appear to prove the efficiency of the proposed technique, and they will continue to be more thoroughly investigated.

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