The Neutralization-Flocculation-Lamellar Settling (NF-LS)process in the treatment of Acid Mine Drainage (AMD) from Coal Mines in South Brazil. Comparative processes and new basis for sulphate ion removal

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Abstract Coal mining activities readily generate acid wastewaters after contacting pyrite with air and water (superficial or subterranean) resulting in AMD-Acid Mine Drainage, loaded with heavy metal ions at pH < 3. This paper summarizes results of treatment processes composed of neutralization-flocculation (NF) and flocs/water separation in lamellar settler (LS) or by flotation with microbubbles (DAF-dissolved air flotation). Furthermore, the works presents a new basis for sulphate ions removal by co-precipitation of this pollutant with aluminum salts. Two AMD from different coal mines were used as models, characterized by their content, namely inorganic or organic elements, suspended and dissolved solids, among others. After neutralization of the AMD, the precipitates are then flocculated using a cationic polymer flocculant in a specially designed flocculation reactor, patented by this research group (FGR®). The separation of flocs in a settler (neutralization-flocculation-lamellar settling-NFLS) showed a high efficiency (>90%) in removal of ions, lower power requirement and process simplicity than when DAF was used. Flocs settled at rates of the order of 5—6 m.h-1 and operating costs for the AMD treatment at pH 9 were estimated to be around $ 0.3.m^{-3}. The treated water was nearly free of heavy metals ions, low BOD and TOC, low solids content and no fecal coli forms, making it useable for irrigation, and other purposes. It is concluded that this research will contribute in the discussion of this old and complex problem in acid mining effluents worldwide. Sulphate ions are, in one case precipitated, at pH 12, in the form of ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$) formed in situ after reaction with Ca/Aluminum salts. The solid formed was separated off by DAF process. Results showed residual concentrations of sulphate ions lower than 250 mg.L^{-1} and almost 90% removal of ions and solids. Sulphate ions removal in acid medium (pH 4.5) is currently underway and initial results were quite high after co-precipitation-filtration with aluminum salts and solids separation either by LS or DAF.

Key Words Acid Mine Drainage, lamella settler, sulphate ions, water reuse

Introduction

Coal AMD-acid mine drainage treatment using neutralization, flocculation and solid/liquid separation by dissolved air flotation-DAF or by lamella settling-LS are now in progress in Brazil. An extensive research between these processes has been conducted by the last four years (Rodrigues and Rubio, 2007, Rubio et al. 2009). Results showed some advantages (simplicity and operating costs) of lamella settling over DAF at the solid/liquid separation. Yet, no great differences were found in terms of pH, metals ions removal and water quality to urban and agricultural reuse. Conversely, sulphate ions have shown to be very difficult to remove, technically and economically despite the fact that this anion causes several environmental problems worldwide (INAP, 2003; Cadorin, 2007; Rubio et al., 2009). In fact its removal from wastewaters constitutes a real challenge in many industries.

The pilot plant units studied were very compact, this mainly because in the flocculation stage the conventional system (tanks with mechanical or pneumatic stirring) has been changed by a new rapid hydraulic flocculation device, the FGR-flocs generator reactor. Thus, the system, which occupied a very small foot print, follows by flocs flotation and/or flocs settling stages (Rubio and Carissimi, 2005). In this research FGR was employed with or without injection of bubbles used to generate two types of flocs, aerated or not, and evaluates two different flocs/liquid separation techniques. More, this work contributes to the international discussion on more efficient (rapid and cheaper) AMD treatment processes.

Methods

A heavy (high ionic force and acidity) and a light loaded AMD´s were studied in detail. Lime was employed for the AMD neutralization and metal ions precipitation and a high molecular weight cationic polymer supplied by SNF/Floerger® was utilized to generate flocs. Flocculation of precipitates was carried out in a special flocculator, FGR® (Rubio and Carissimi, 2005, Rubio et al. 2009) using velocity gradient (G value) of about 1000 s^{-1} to ensure good flocculant dispersion and flocs growing.

High Rate Flotation (HRF) and lamella settling (LS) studies were conducted at room temperature over a period of 8 months, covering summer and winter. In the flotation studies, sodium oleate was added to enhance the flocs hydrophobicity and process kinetic. A small pilot unit treating about 1–1.5 m^3h^{-1} (Fig. 1a) with the feed being collected into two 2 m^3 fill tanks (pH adjustment).

A centrifugal multiphase (water/air) pump (Edur®) was used to disperse, dissolve and saturate air in water and microbbubles generation. Inclined lamellas inside the flotation tank were used to enhance floc-flotation recovery and a porous plate at the bottom of the tank was employed allowing a smooth flow of the treated water at the outlet (in a laminar hydrodynamic regime).

Studies of lamellar settling (Figure 1b) were conducted at pH 7 and 9, using lime, 10 $mg.L^{-1}$ of Flonex and 1 m^3h^{-1} feed flow rate.

For the sulphate removal, aluminum salts are conditioned in a conditioning tank at pH 12 (ettringite precipitation) or pH 4.5 for the co-precipitation of the anions onto aluminum colloids. Results found showed a great expectation in the local coal industry mainly due to the more rigorous environmental laws.

Results

The physical-chemical characteristics of (soft and heavy) acid mine waters are shown in Table 1. Figure 2 shows results of Fe and Mn ions removal in soft AMD at pH 9 using separation of flocs by either lamellar settling or flotation. All results show high and similar efficiencies reaching removal values higher than 90% for all metal ions. Results obtained at pH 7 were similar with pH 9, except that the Mn removal due to the incipient precipitation of manganese hydroxide at that pH. Sulphate ions removal at pH 12 and aluminum salts conditioning was carried out by DAF process. Results showed a very low residual concentrations of sulphate ions (< 250 $mg.L^{-1}$) and removal of ions and solids of the order of 90%. However, operating costs may reach $ 3.40 (USA) per one cubic meter of soft AMD and this is considered very costly and more research has to be put to reduce this value.

Treatment of heavy AMD also was carried out using LS process for the solid/liquid separation. Again, best results were found at pH 9 due to the Mn removal. Figure 3 shows results found in the NFLS studies focussing on removal of iron, manganese and sulphate ions. Water quality is considered of good quality for reuse in many activities.

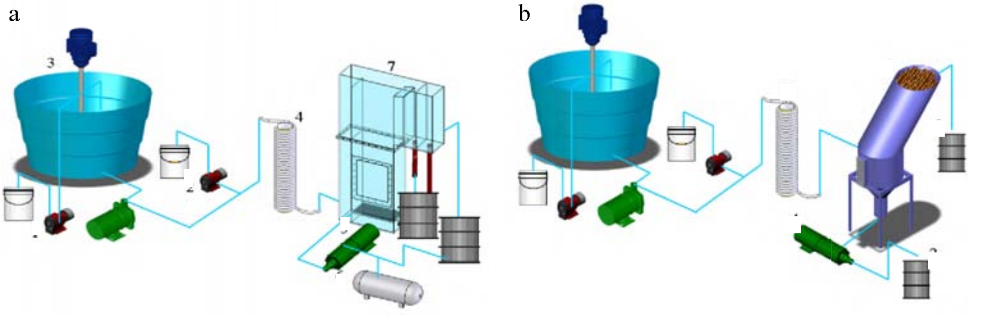

Figure 1 a) Unit pilot scale to treatment of acid water (sulphate and metals ions removal) – Criciúma/SC (≈ 1 m^3h^{-1}); b) Lamella settler unit (≈ 1—1.3 m^3h^{-1}) to treat AMD heavily and softly loaded-South Brazil). LS (lamella settler-with inside tubes); Treated water to reuse; FGR (Flocs Generator Reactor – helical shape)

***Table 1** Acid Mine Drainage from coal mines in south Brazil, average of main parameters*

Parameter	Soft AMD	Heavy AMD
pH	3	2.5
Sulphate ion, mg.L^{-1}	1,000	11,500
Fe, mg.L-1	4.5	1,900
Mn, mg.L-1	2.7	12.5

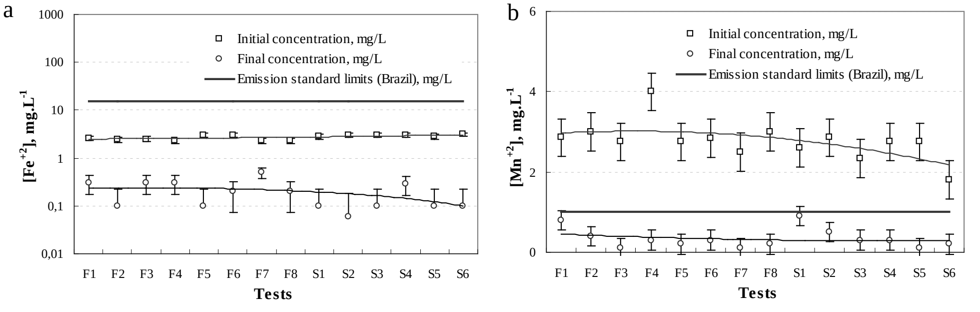

***Figure 2** AMD (light) treatment, at pH 9, and flocs separation by either flotation or lamellar settling. a) Removal of Fe ions; b) Removal of Mn ions*

Sulphate ions removal in acid medium showed to have high potential after precipitations of tghe anions with aluminum bearing salts.

Figure 4 (a and b) shows a very low final sulphate concentration at 7:1 and 10:1 mass ratio, between coagulants ($AlCl_3$ and PAC, respectively) and sulphate (mg.mg^{-1}) and a high efficiency (peak) at pH 4.5. The final sulphate ion concentration was < 250 mg.L^{-1}, which correspond to the drinking water standard limit in Brazil (for an initial concentration of 1800 mg.L^{-1}. The recommendation for the emission limit from the World Health Organization (500 mg.L^{-1}) was attained using a 5:1 and 8:1 mass ratio to $AlCl_3$ and PAC, respectively.

Some countries and international organizations such as the EPA (Environmental Protection Agency), have defined quality standards when reusing the water from treated domestic sewage treatments. For industrial wastewaters in Brazil, there is no legislation regarding the reuse or recycle. A number of non potable alternatives (usages) for treated water as urban, agricultural, forestry, industrial and aquaculture purposes has been suggested by Brazilian laws but physical-chemical parameters has not been ruled yet.

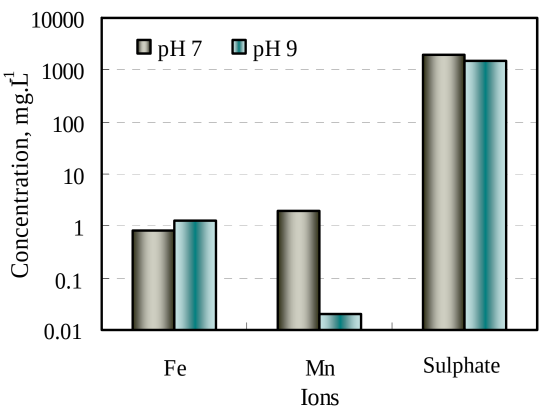

***Figure 3** AMD (Heavy) treatment by NFSL. Removal of Fe, Mn and $SO_4{}^{-2}$ ions at pH 7 (a) and 9 (b)*

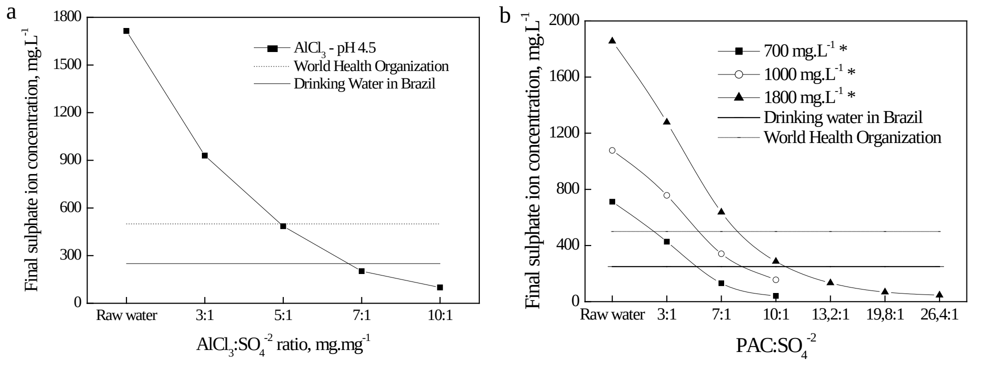

Figure 4 *Sulphate removal in acid medium (pH 4.5) using $AlCl_3$ (a) and PAC (b) coagulants at pH 4.5. Synthetic solutions with Na_2SO_4*

The research continues and an installation of a NFLS plant is being constructed, aiming at recycling the treated water in, among others, pavements, streets and vehicles washing and dust control. Other uses will depend on legislation authorization.

Conclusions

Results showed that a FGR was very effective in producing rapid settling and flotation yielding strong flocs. The unit LS 1–1.3 $m^3.L^{-1}$ was fairly compact and reached a loading capacity of approximately 5–6 $m.h^{-1}$. NFLS process presented lower operating costs than NF-DAF process, both showing high removal of metal ions (>90%). Best results (NFLS) were found at pH 9 providing a good quality of the treated water: i.e., heavy metals free, low BOD, low TOC, among others (color, turbidity) and an operating cost of around \$ 0.3 m^{-3}. Sulphate ions were removed, at pH 12, after ettringite precipitation with Al salts and DAF of the flcos generated. The final concentration of sulphated attained was lower than 250 $mg.L^{-1}$ (the drinking water standard limit in Brazil) but operating costs were very high and poses a challenge to mining industry. Preliminary results of sulphate removal at pH 4.5 showed efficiencies higher than 85% using PAC and $AlCl_3$ at 10:1 and 7:1 ratio. It is concluded that this research will contribute in the discussion of this old and complex problem in acid mining effluents worldwide.

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