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Treatment and water reuse of lead-zinc sulphide ore mill wastewaters by high rate dissolved air flotation

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ABSTRACT

Simulated wastewaters (concentrate and tailings thickener overflows), from a future lead-zinc flotation separation plant, were treated for the removal of target metal ions (Zn^{2+}, Pb^{2+} and Cu^{2+}) and suspended solids (0.1–0.5 g L^{-1}). The ions were adsorbed onto ferric hydroxide precipitates, and then removed by dissolved air flotation (DAF). Best results obtained at bench scale were validated at pilot scale, employing i. 15–20 mg L^{-1} Fe^{3+} (chloride salt); ii. Flocculation in two units (rapid mixing - G > 120 s^{-1}, and slow mixing - G = 20–80 s^{-1}), with 0.2–0.5 mg L^{-1} of flocculant (a cationic polyacrylamide); iii. DAF at a saturation pressure of 6 bar and a 20% water recycling rate. The removal of ions between pH 6.5 and 7.5 was very high, reaching separation efficiencies up to 95% for Pb^{2+} and Cu^{2+} ions (potential activators of ZnS); the adsorption mechanisms of the uptake of the ions were discussed. The suspended solids (fine particles, < 44 µm) were separated by DAF (89–96%) to concentrations < 0.5 g L^{-1}. For higher solid contents, the formed flocs became larger, difficult-to-float and operating conditions required less flocculant and a higher recycling ratio. These high separation efficiencies allowed reuse of water in the lead/zinc sulphide ore rougher flotation stage, avoiding the activation of ZnS flotation. The pilot DAF unit (1.8–2.4 m^3 h^{-1} flow rate) followed an innovative design by enhancing the height/area rate (6.9 m^{-1}), compared to conventional cells; it included specially designed and oriented lamellae and a perforated plate to control internal turbulence. These modifications allowed the enhancement of the hydraulic loading capacity up to 15 m^3 m^{-2} h^{-1} (or 15 m h^{-1}), more than double the known value for conventional DAF cells (about 7 m h^{-1}). Estimations of general costs for a 300 m^3 h^{-1} treatment plant were calculated and the operating costs reached US\$ 0.56 m^{-3} of treated water. It is believed that this DAF process has a high potential for removing deleterious ions from water at a high removal rate, recycling process water feeding ore flotation plants and minimizing effluent discharge (sometimes polluted).

1. Introduction

Mining and mineral processing employs large quantities of water and produces aqueous effluent suspensions containing harmful pollutants that contaminate environmental ecosystems. As they are transferred and enriched in superficial water or soils, they affect crops (acid or alkaline soils) and eventually contaminate animal bodies while drinking (Dunne, 2012; Gunson et al., 2012; Mohd Udaiyappan et al., 2017).

These effluents might not be reutilized, in mineral processing unitary operations, without treatment due to the presence of metal ions, anions, organic matter, bacteria, residual flotation collectors or high suspended solids content (Kang et al., 2017; Liu et al., 2013; Rao and Finch, 1989; Rao et al., 1988; Rodrigues and Rubio, 2007; Rubio et al., 2002a; Zhang and Zhang, 2012).

Accordingly, there is fast-growing concern for stricter regulation for mining water management, focusing on the minimization of fresh feed water and effluent discharge (Dunne, 2012). Moreover, there is an increasing demand for water reuse practices caused by resource shortages and environmental protection. Improvement of wastewater cyclic utilization and the reduction of waste emissions are considerable challenges and urgent tasks in modern mining (Freire–González and Font Vivanco, 2017).

Additionally, accidents involving tailing dams are known and have forced companies to consider concepts of dry mining (waste and tailings disposal) and water reclamation (Burritt and Christ, 2018; Gunson et al., 2012; Ihle and Kracht, 2018).

Froth flotation, the most important high rate process in ore

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beneficiation, operates with high volume of water along the many ancillary operations, namely: grinding, screening, wash water, dust suppression, pump gland seal water and reagent make up. In practice, fractions of these wastewaters return to the flotation mill after natural settling in tailings dams or flotation product thickening.

Due to the cyclic enrichment of deleterious chemical compounds, flotation requires good quality water, as some specific ions, colloids and suspended solids readily interfere in the mechanisms of bubble-particle interactions, pulp rheology and froth stability. Thus, there is a need to reduce the concentration of ions which might cause activation of gangue particles, decrease the separation selectivity and create froth problems (stabilization) (Bıçak et al., 2012; Chen et al., 2009; dos Santos et al., 2010; Ikumapayi et al., 2012; Liu and Zhang, 2000; Liu et al., 2013; Rao and Finch, 1989; Weedon et al., 2007).

Hence, the treatment of process waters for reuse is often required, but this is not a common practice. Should the removal of ions in low concentrations (< 20 ppm of copper, lead, zinc) be required, separations technologies as flocculation-settling or filtration (micro or nano) will not be effective. Herein, the dissolved air flotation (DAF) of an ion-loaded carrier becomes a competitive alternative.

DAF is a well-known process in water and wastewater treatment (Crossley and Guiraud, 2016; Edzwald and Haarhoff, 2011; Edzwald, 2010; Edzwald and Becker, 2012; Edzwald and Han, 2007; Kiuru and Vahala, 2000). This process efficiently removes a number of pollutants, such as colloidal, fine and ultrafine particles, organic and inorganic precipitates, ions, microorganisms, proteins, dispersed and emulsified oils in water (Lazaridis et al., 1992; Liu et al., 2012; Oliveira and Rubio, 2009; Rubio et al., 2007, 2002a;Tessele et al., 1998).

In dissolved air flotation (DAF), water saturated with air under pressure (> 3 bar) passes through a nozzle (flow constriction) whereby the bubblesare formed and reach the flotation chamber, at atmospheric pressure. Then, the supersaturated water is forced trough needle-valves, venturi-type tubes or special orifices, and clouds of bubbles are produced just down-stream of the constriction, floating and removing the pollutants (Rodrigues and Rubio, 2007; Rubio et al., 2016, 2002a). The microbubbles generated in DAF have a bubble size distribution within the range of 20–80 μm (Rodrigues and Rubio, 2003).

Yet, recent work has identified and measured the concentration of nanobubbles, which are formed simultaneously with the microbubbles in DAF systems (Azevedo et al., 2016a; Etchepare et al., 2017c). The bubbles size distribution of these nanobubbles varied within the range of 50–800 nm and has been found that these bubbles assist, not only flotation with microbubbles for wastewater treatment, but also the ore flotation where big bubbles (1–2 mm diameters) are employed. The mechanisms involved are: i. The nanobubbles serve as nuclei for other bubbles to attach onto particles; ii. They aggregate ultrafine particles and colloidal precipitates, and iii. They assist for the formation of light aerated flocs (Azevedo et al., 2016b; Calgaroto et al., 2015; Rubio et al., 2016).

A well-known industrial technique is the use of an ion adsorbing precipitate followed by flotation withmicrobubbles. This technique has been called APF or ACF, for adsorbing particulate (or colloid) flotation (Capponi et al., 2006; Huang and Liu, 1999; Lemlich and Arod, 1972; Rubio et al., 2002a). Flocculation is sometimes required to reduce the amount of precipitates, to withstand mechanical resistance of the flocs formed and to increase the air-to-solids ratio, to increase process efficiency, especially kinetics (Rodrigues and Rubio, 2007; Rubio et al., 2016, 2002a).

The main carriers employed are ferric or aluminium hydroxides, sometimes using sodium oleate or lauryl sulphate as collectors to improve flotation kinetics. These reagents eliminate the use of flocculants (Capponi et al., 2006; Lazaridis et al., 1992; Rodrigues and Rubio, 2007; Rubio et al., 2002a; Stalidis et al., 1989).

Although DAF applications in the mining industry are still scarce, some research studies have demonstrated their potential in many areas, namely: i. Acid mining drainage treatment (Cadorin et al., 2007); ii. Removal of sulphate ions (Amaral Filho et al., 2016); iii. Treatment of process water from concentrate filters, overflows of thickeners and drainage from tailings disposal (Al–Thyabat and Al–Zoubi, 2012; Azevedo et al., 2016b; Calgaroto et al., 2016; Couto et al., 2011, 2014).

Industrial DAF operations have been commissioned in Chile for more than 18 years, probably because the arid northern region of Chile requires large needs of water sources in mining and mineral processing operations. This situation has pressed the industry towards the use of seawater, which is expensive because mines are located in regions of high altitude, distant from the coastline. Thus, alternatives such as DAF have been introduced to reduce water consumption by means of reuse (or recycling), saving freshwater and minimizing mine water discharge (Alhucema et al., 1997, 1996; Liu et al., 2013; Ramírez et al., 2015; Rodrigues and Rubio, 2007).

Up to the present knowledge, DAF plants in mining industry are only encountered in Chile, mainly treating Cu/Mo concentrate filter wastewaters and overflows of thickeners of copper concentrates. The treated water is being reutilised in flotation mills, water services (dust suppression, machine and truck washing) and for local irrigation.

Main plants are the following (Alhucema, 2018):

i. Punta Chungo: DAF unit treating 108 $m^3 h^{-1}$ of water from Cu/Mo concentrate filter to remove suspended solids and ions (metal ions, sulphide and molybdate), some fairly deleterious for water irrigation (contamination of plant growing). More, the molybdate anions cause molybdenosis, a disease of ruminants after intake of excessive molybdenum. The treated water, by DAF, has the quality suitable for reuse in local irrigation, a very dry area.
ii. Collahuasi: 111 $m^3 h^{-1}$ DAF unit treating copper concentrate thickeners overflow water treatment to remove Mo ions, residual sulphide and arsenic ions and ultrafine solids.
iii. Minera Esperanza: DAF plant treating 216 m^3 h^{-1} copper concentrate thickeners overflows removing copper and iron ions, for water reuse.

All these plants employing ferric chloride to form hydroxides to adsorb the harmful ions are quite successfully. Yet, further research examples appear to be needed to validate its feasibility and stimulate its implementation in the mineral sector.

Some advantages of the DAF process are the ability to treat high volumes of effluent (100–600 m^3 h^{-1}), small occupied area, excellent treated water quality, generation of thicker sludge and rapid start up (Capponi et al., 2006; Edzwald, 2010; Féris et al., 2000; Rubio et al., 2002a, 2002b, Rodrigues and Rubio, 2007).

The main disadvantages of DAF are high-energy consumption and high operating costs compared to coagulation-sedimentation-filtration plants. Common operating saturation pressures range between 3 and 6 bar and this stage is usually very costly. Additionally, DAF operation reliability requires some professional skill.

Thus, in order to be more attractive, future DAF installations should seek to enhance process efficiency with modern design. The industrial superficial hydraulic loading capacity, commonly about 7–9 $m h^{-1}$ ($m^3 m^{-2} h^{-1}$) might be more attractive at twice this value. Recent innovations in DAF come with new designs of the particle-bubble contact zone (mushroom type), cell height (higher than older ones) and shape-form (tank or columns) (Rubio, 2002) and the injection of nanobubbles (Azevedo et al., 2016a; Calgaroto et al., 2016; Etchepare et al., 2017a, 2017b).

In this context, this work studied a modified DAF pilot unit for the treatment of a simulated wastewater (concentrate and tailings thickener overflows) of a future lead-zinc sulphideflotation separation system (Nexa Resources, to be commisioned in 2019). Ferric hydroxide precipitates were the carrier for the removal of metal ions (Zn^{2+}, Pb^{2+} and Cu^{2+}). An innovative high-rate DAF cell was designed with inclined parallel lamellae in the separation zone and a perforated plate at the bottom. These modifications aimed to reduce floc settling, optimize