

Neutralization and co-precipitation of heavy metals by lime addition to effluent from acid plant in a copper smelter



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ABSTRACT

The effluents from acid plants generated in copper pyrometallurgy contain high concentrations of sulphates and heavy metals that difficult further reuse of contained water. In this study, the neutralization of an effluent was studied by progressive addition of lime as a pH-modifying agent. Batch and continuous tests were conducted to evaluate the neutralization potential between pH 1 and 11 on an effluent containing As, Cu, Fe, Zn, Ni, Pb, Cd, Hg, Sb, Mn, Mo, Al and SO_4^{2-} . In batch process neutralization, an efficiency of about 99.5% was attained except for Sb 98% and Pb 97%. Similar values were obtained for the continuous mode. The production of gypsum with commercial value was also evaluated based on the Chilean standard for hazardous solid waste measured by the TCLP (Toxicity characteristic leaching procedure) test. Best results were obtained between pH 1 and 2, after a minimum of four washes. The rheology of the residual solids was characterized using filtration tests and the sedimentation rate determined with different flocculants. The final liquid effluent was evaluated by the ASTM corrosion test and showed a non-corrosive nature, with a corrosion rate of 0.07 mm/year, well below the value allowed by established standard of 6.35 mm/year.

1. Introduction

In Chile, the control of industrial liquid waste (LW) has taken increased importance in large and medium-sized mining companies that process copper ores. These companies have to comply with environmental standards for adequate neutralization of their solid wastes (DS N° 148, 2004) and the urgent need to recover and reuse water.

The giant porphyry copper deposits are located in the driest regions in the world (Cooke and Hollings, 2005) and require ever increasing volumes of water for mining and mineral processing. Table 1 shows that in 2016, 72.9% of the water used in copper mineral processing corresponded to recirculated water, a 23.0% of fresh water and 2.7% of seawater, required to complete the requirements that rise to 1870 million m^3 /year (Cochilco, 2017).

The pyrometallurgical processes that allow copper to be recovered from sulphides take place in a series of successive stages, most of which operate at high temperatures (typically 1250–1350 °C, depending on the type of reactor used). The smelting, conversion and refining stages generate gases rich in SO_2 as a result of the progressive oxidation of the sulfur contained in the copper concentrates, mainly in the form of copper and iron sulphides. The treatment of these gases to fix the SO_2 ,

preventing it from being released into the atmosphere, through the production of sulfuric acid, generates a liquid effluent (LW). This LW from Cu smelters has its origin specifically in the gas cleaning plant designed to capture SO_2 produced during the smelting and conversion of sulphide concentrates of Cu (Valenzuela et al., 2003), which consist mainly of chalcopyrite (CuFeS_2), chalcocite (Cu_2S), digenite (Cu_9S_5), covellite (CuS) and bornite (Cu_5FeS_4). However, some Cu sulfosalts such as enargite (Cu_3AsS_4), luzonite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) and tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) contain significant amounts of As and Sb.

Pyrometallurgical smelting and converting processes have proven to be highly selective for Cu but not for heavy metals. Studies by Steinhäuser et al. (1984) using a flash furnace for melting copper concentrates indicate that the volatilized fraction corresponds to 80 wt % As, 80 wt% Bi, 70 wt% Pb, 40 wt% Sb, 40 wt% Zn, 20 wt% Se and 5 wt% Ni. These metals circulate in the gas handling-cleaning system and part of them remains in the acid produced, a small fraction is emitted, some are retained in the flue dust and the rest is contained in the effluent from the acid plant.

During the neutralization step of the acid effluent the use of a number of reagents was evaluated, including: soluble silicate and kiln dust (Conner and Hoeffner, 1998), calcite (Papassiopi et al., 1996),

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Table 1
Water consumption for Chilean copper production (2016).

Water type	Flow, m ³ /s	%
Fresh water	13.6	23.0
Seawater	1.61	2.70
Desalinated seawater	0.83	1.40
Recirculated water	43.3	72.9
Total	59.3	100

Table 2
Chemical characterization of the LW, Level 1 and Level 2.

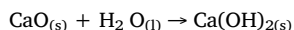
Analysis	Concentration		Unit
	Level 1	Level 2	
As	689	1388	mg/L
Zn	2832	5653	mg/L
Ni	26	50	mg/L
Pb	46	89	mg/L
Cd	162	327	mg/L
Hg	41	82	mg/L
Sb	16	30	mg/L
Cu	1325	1322	mg/L
Fe	167	170	mg/L
Mn	16	18	mg/L
Mo	21	22	mg/L
Al	65	63	mg/L
SO ₄ ²⁻ ^a	74	75	g/L
Cl	2798	2792	mg/L

^a gravimetric analysis (BaSO₄ precipitation).

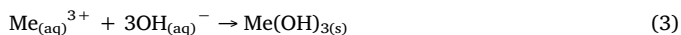
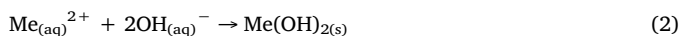
caustic soda (Papassiopi et al., 1996; Eslamzadeh et al., 2004), lime (Navarro et al., 2004), dolomite and fly ash (Potgieter-Vermaak et al., 2006), limestone (Potgieter-Vermaak et al., 2006; De Beer et al., 2008; Silva et al., 2012), FMBO (1:1)-diatomite¹ (Chang et al., 2010), Mn and Fe solutions (Deschamps et al., 2005), Portland cement, phosphate and magnesium oxide (Navarro et al., 2011).

However, lime (CaO) represents the most economical and efficient alternative for the neutralization of cations dissolved in LW, either as hydroxides or complex anions (Zinck, 2005), due to its low cost and insensitivity to temperature fluctuations (Khorasanipour et al., 2011).

The neutralization and co-precipitation process proposed begins with the hydrolysis of lime (1), followed by its partial dissolution resulting in a pH increment due to the formation of hydroxyl ions (2).



Then, the hydroxyl ions follow a series of interactions with divalent and trivalent cations present, represented in a general form by reactions (2) and (3), which may, pH < 11.3, involve simultaneous precipitation of gypsum (4), if any free sulphate exists.



The objective of this work was to show the development and implementation of a neutralization circuit using lime for acidic effluents from gas treatment plants of smelting-converting processes of sulfide copper concentrates. This allows the neutralization of sulfuric acid and the simultaneous precipitation of metals such as As, Al, Cd, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb and Zn, in compliance with the health regulations on hazardous waste management (DS N° 148, 2004) as assessed by the US-

EPA Toxicity Characteristic Leaching Procedure TCLP (USEPA, 1991). In addition, rheological characterization of the waste by tests of sedimentation, filtration and corrosion was also carried out for proper recovery and reuse of water in the process.

Although the method exposed here is, in general, known and commonly used for the treatment of liquid effluents, in this paper, not only the evaluation of this method in the removal of heavy metals and other contaminants from industrial liquid waste is presented, but also the possibility of producing a good quality gypsum as a byproduct with potential to be used as flux during the operation of the smelting and converting furnaces, is discussed.

2. Materials and methods

2.1. Characterization of the LW

The LW used in the tests came from a single absorption acid plant in a copper smelting process. The original LW (as received and adjusted previously test to historic level) had a concentration called Level 1. In order to study the effect of a drastic increase in the concentration of cations that may occur in the plant, a synthetic LW called Level 2 was prepared with twice the concentration of the species of LW Level 1 which vary most in the plant such as As, Zn, Ni, Pb, Cd, Hg and Sb. The concentration of the other elements does not vary significantly in plant, so these were unchanged. Each of the solutions (Level 1 and Level 2) was analyzed by atomic absorption and gravimetric methods. Table 2 shows the chemical characterization of both levels.

Similarly, the residual solutions in each of the neutralization stages were analyzed. The lime used was analyzed by digestion followed by AAS (Atomic Absorption Spectrometry) and the results are shown in Table 3.

2.2. Mineralogical characterization of the solids

The mineralogical characterization of solid obtained in the neutralization and precipitation process was performed by X-ray diffraction (XRD) using a Bruker D4 Endeavor® operated with Ni-filtered and Cu radiation.

2.3. Neutralization tests

Neutralization tests were performed in a pilot plant with two 100 L tanks connected in series. These tanks have conical bottom and variable speed agitators, also a lime conditioning tank of 50 L and peristaltic pumps for propelling LW and lime suspension. Furthermore, the pilot plant has two vacuum filters 30 cm in diameter and two pH meters. Both tanks operate in series and continuous configuration to simulate two stages of neutralization at room pressure and temperature (101.4 kPa and 25 °C in Concepción, Chile). During the neutralization tests, submerged thermocouples were used to constantly monitor the liquid temperature in the tanks and provided the input to the temperature controller which regulated the flow of the heat exchanger fluid in the external cooling jackets of the three tanks. Fig. 1 shows the configuration of the in series tanks.

2.4. Sedimentation test

Tests were conducted to determine the sedimentation rate of the precipitates in a 0.5 L pulp sample at acidic and basic pH. Three doses of flocculants were evaluated in each case. The reagents used were: Superfloc A110, Preastol Magnafloc 6260 and 2620. Flocculants were prepared in solution by mixing 0.5 g of flocculant and 0.4 L of water with stirring at a low intensity for 2 h to ensure complete dissolution.

¹ Fe-Mn binary oxide incorporated into diatomite (1:1).

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