



Acid curing and agglomeration for heap leaching

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ABSTRACT

The impact of acid treatment in agglomeration/acid curing on copper extraction and acid consumption was investigated with respect to acid dosage and moisture. Without the addition of water, no agglomeration occurred. At an acid dosage above 15 kg/t, the acid was not completely consumed during acid curing. With the addition of a suitable amount of water, the particles well agglomerated together. Copper, iron, magnesium and manganese were dissolved as sulfates and concentrated in the fine fraction of the ore. The copper extraction and net acid consumption increased with increasing acid dosage. The copper extraction for acid curing with the addition of 6.2% water was higher than that without the addition of water due to the improved permeability of a heap and the increase in the water-soluble copper. During acid curing, the reaction of sulfuric acid with muscovite, albite and nacrite mainly took place on the surface of the particles while the reaction of sulfuric acid with clinocllore occurred not only on the surface but also through the particles. This work contributes a case study to the body of knowledge on curing/agglomeration, which is currently relying essentially on empirical trial-and-error adjustment of conditions in practice. Further investigation is needed to develop fundamental understanding of acid curing and agglomeration for better operating practice.

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1. Introduction

Acid curing and agglomeration are generally used prior to heap leaching of copper oxide and secondary sulfide ores to improve the copper extraction process. Agglomeration is used to bind fine particles to coarse ones to increase the permeability of an ore heap while acid curing inhibits the dissolution of some silicates and accelerates copper extraction.

Nearly all silicate structures can be classified as the following six groups: (1) independent tetrahedral structure (SiO_4^{4-}), (2) double tetrahedral structure ($\text{Si}_2\text{O}_7^{6-}$), (3) ring structure ($(\text{Si}_3\text{O}_9)^{6-}$, $(\text{Si}_4\text{O}_{12})^{8-}$ and $(\text{Si}_6\text{O}_{18})^{12-}$), (4) chain structure ($(\text{Si}_3\text{O}_9)^{6-}$ and $(\text{Si}_4\text{O}_{11})^{8-}$), (5) sheet structure $(\text{Si}_2\text{O}_5)^{2-}$ and (6) three dimensional network $(\text{SiO}_2)_n$. The action of acids on a silicate produces one of the following results (Terry, 1983a): (1) complete breakdown of the silicate structure, resulting in the dissolution of metal cations and silica and the formation of silica gel due to polymerization of silica in aqueous solution, (2) partial decomposition of the silicate structure, leading to the dissolution of cations and leaving a siliceous residue, (3) no reaction. The first three structures are prone to acid decomposition and dissolve. The infinite structures (chain, sheet and framework) are not easily broken down into smaller silicate units and generally partially dissolve leaving siliceous residue. If aluminum or ferric iron replaces silicon in the structure,

the strength of the infinite structure weakens and leads to a greater susceptibility to acid attack (Murata, 1943; Terry, 1983a). The equilibrium solubility of amorphous silica is very low. However, a supersaturated solution can be formed and the silica polymerizes to produce a silica gel. The formation of a silica gel can have serious consequences in the subsequent processing of the leach liquor. In heap or dump leaching, a gelatinous precipitate may blind the ore particles and result in poorer leaching kinetics and recoveries. Gel formation can also severely hinder subsequent solvent extraction, ion exchange and electrolysis stages.

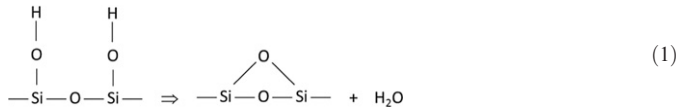
Dehydration of polymeric silica results in precipitation of amorphous silica to prevent the formation of silica gel by (1) starving the solution of water, (2) employing strong acid solution at or above boiling point, and (3) precipitation procedures at high pressure and temperature (Terry, 1983b). Acid curing is a pretreatment in which concentrated sulfuric acid is added to a crushed ore to start reactions with acid soluble metals and gangue minerals to inhibit the formation of silica gel by dehydration.

Although acid curing and agglomeration are used in commercial heap leaching of copper, there is very little systematic information available. The practice of acid curing and agglomeration seems to fall largely in the realm of experience and practice. The optimized conditions of acid curing and agglomeration (acid requirement, crushed ore particle size, curing requirement-weak or strong curing, and moisture) are dependent on the size distribution of gangue and copper minerals and the overall mineralogy (Baum, 1999). Mineralogy analysis provides data to set conditions for acid curing and agglomeration.

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From the literature, the moisture content of the ore for agglomeration is in the range from 5 to 10% while the time for acid curing is generally one to five days (Alvarez et al., 1996; Cruz et al., 1980; Lindsay, 1994; Pazour, 1981). Acid curing caused dehydration of some silicate minerals (Reaction 1), inhibiting the silicate dissolution (Iler, 1979). The absence of the hydroxyl group renders the surface hydrophobic and virtually insoluble in aqueous solution. Under the conditions of acid curing and agglomeration, the copper extraction rate is improved by the sulfation of copper ore, there is an enhanced permeability of the ore and a reduction of competition for acid by passivating the acid-consuming gangue.



At the Zaldívar mine site in Chile, 150,000 tons per year of copper is recovered by heap leach – SX/EW process (Zaldívar, 2016). The crushed ore is treated by agglomeration and acid curing prior to heap leaching.

The objective of this study was to investigate the impact of acid curing/agglomeration of the Zaldívar ore on copper extraction and acid consumption,

2. Experimental

The agglomeration was conducted in a 25-L plastic bottle, which was placed on a 20°-inclined bottle roller. The ore was first placed into the bottle and then fed with a required amount of water during tumbling. Concentrated sulfuric acid (98%) was successively added after 15 s at four acid dosages of 5, 10, 15 and 20 kg/t respectively. After 5 min of tumbling, the ore was transferred into a sealed bucket for 2 weeks of acid curing.

The acid-cured ore was placed in a column holding 5 kg of ore. After flushing the loaded column using argon to remove oxygen, the feed solution was pumped through the column from its bottom to top using a peristaltic pump, and then the over-flow was collected in a sealed bucket. The flow rate was adjusted to 14.2 L/h/m² and it took 9 days to pass 25-L feed solution through the column.

The column was made of ABS plastic material. The inside diameter and height of the column were 10.2 and 59 cm respectively. A perforated disk was placed near the bottom to support the ore. The distance between the disk and the column bottom was 2 cm. Glass fiber was placed on the perforated disk to prevent the fine particle from falling and blocking the flow. A perforated disk was also placed on the top of the ore and there was a layer of glass fiber between the perforated disk and the ore so that the fine particles were blocked by the glass fiber to prevent any elutriation of fines out of the ore bed.

The particle size distribution of the Zaldívar ore sample received from Placer Dome (now Barrick Gold) is given in Table 1. The free water content was 0.3%. The chemical composition is summarized in Table 2.

This feed solution was prepared using deionized water, technical grade aluminum and magnesium sulfates, reagent grade sodium chloride, manganese sulfate and sulfuric acid. The solution pH was adjusted to 1.5 by adding a 2 M sulfuric acid solution. Finally 10 mL of 2% thymol solution was added as bactericide. The feed solution composition was 20 g/L Al, 18 g/L Mg, 1.2 g/L Mn and 1.3 g/L Cl, which was a typical solution composition after the copper solvent extraction at the Zaldívar plant site. The leached ore was filtered and washed with deionized

Table 1
Particle size distribution of the Zaldívar ore.

Size (mm)	<0.3	0.3–0.85	0.85–2.0	2.0–3.35	3.35–6.3	6.3–9.5	9.5–12.5	>12.5
Distribution (%)	10.0	9.66	5.76	7.32	18.63	17.04	13.17	18.42

Table 2
Contents of the main elements (%) in the ore.

Elements	Cu	Fe	Ca	Zn	Mg	Mn	S ²⁻	S(SO ₄ ²⁻)
Feed bulk	1.19	2.88	0.49	0.032	0.56	0.022	–	–

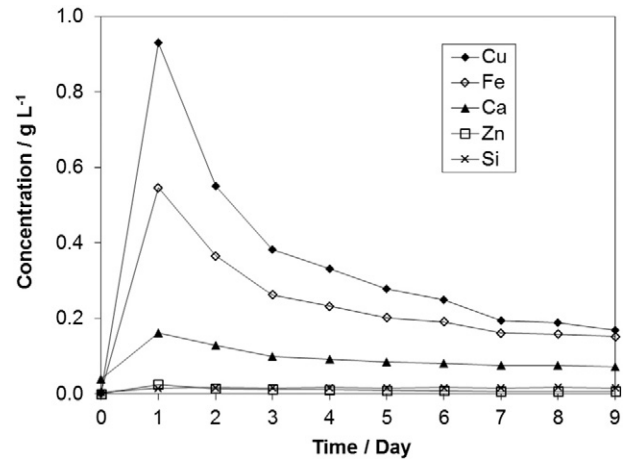


Fig. 1. Concentrations of copper, iron, calcium, zinc and silicon as a function of time at a sulfuric acid dosage of 15 kg/t.

water using Whatman No. 42 filtration paper. The samples were analyzed by ICP (Inductively Coupled Plasma).

3. Results and discussion

3.1. Agglomeration and acid curing without the addition of water

Without the addition of water, very little agglomeration occurred after acid curing for two weeks. This suggests that a minimum moisture level is necessary for effective agglomeration. Without the addition of water, such a small amount of sulfuric acid could not be uniformly distributed in the ore since the ore was only partially wetted by sulfuric acid. Some particles were not contacted with sulfuric acid. No gelatinous silica was produced or the surfaces of the particles were not activated to chemically cement particles for agglomeration.

At an acid dosage of 15 kg/t, the concentrations of copper, iron, calcium and zinc in the over-flow reached their maximum values in the first day and then decreased while the concentration of silicon was around 16 mg/L and it practically did not change with time (Fig. 1). Most of water-soluble copper, iron, calcium and zinc were dissolved and flushed from the column in the first day. Similar results were obtained at acid dosages of 5, 10 and 20 kg/t. A higher acid dosage resulted in generation of more water-soluble copper, iron, calcium and zinc in the leachate. The concentration of silicon did not change significantly with acid dosage.

The solution pH vs. time is shown in Fig. 2. At 5 kg/t of sulfuric acid, the pH first increased to a maximum value (1.57) and then decreased. After 3 days, the pH stabilized at approximately 1.54, which was only higher than the feed solution pH by 0.04. At 10 kg/t of sulfuric acid, the pH increased by 0.04 in the first day and then stabilized at 1.53. At 15 kg/t of sulfuric acid, the pH decreased to 1.44, then increased slowly and finally stabilized around 1.52 after 6 days. At 20 kg/t of sulfuric acid,

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