An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions

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ABSTRACT

Copper oxide minerals are normally extracted by acidic leaching followed by copper recovery with solvent extraction and electrowinning. However, copper oxide deposits often containing large amounts of acid consumable gangue leads to a very high acid consumption. In addition, if the oxide deposit also contains precious metals and iron bearing minerals, significant (lime) neutralisation costs are incurred to establish the conditions for subsequent cyanidation, with concomitant production of gypsum, potential formation of silver-locking jarosites and potential gel formation when acids interact with layer silicate minerals. In this study, an alternative aqueous alkaline glycine system has been employed to evaluate the batch leaching behaviour of copper oxide mineral specimens of the minerals azurite, chrysocolla, cuprite and malachite. The effects of glycine concentration and pH were investigated at ambient temperature and atmospheric pressure. Glycine concentration and pH both had a major effect on the copper extraction. Complete extraction of copper from azurite was achieved in <6 h when glycine to copper ratio was 8:1. However, further investigation established the optimum leaching conditions as being pH 11 and glycine to copper ratio of 4:1. Under such conditions 95.0%, 91.0%, 83. 8% and 17.4% of copper was extracted after 24 h from the azurite, malachite, cuprite, and chrysocolla mineral specimens respectively. While the dissolution rates of the copper oxide minerals are markedly slower than acid leaching, the selective dissolution of copper over acid-consuming gangue minerals shows much potential. It was shown through UV–Vis spectroscopy that dissolved copper is in the cupric state and forms a neutral copper-glycinate complex under alkaline conditions. The study has shown that copper extraction from malachite, azurite and cuprite in aqueous alkaline glycine solutions is fast, whereas Cu extraction from chrysocolla was found to be poor and slow.

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1. Introduction

The continuous depletion of large, high grade copper sulfide deposits which are traditionally processed by pyrometallurgical routes requires innovative hydrometallurgical approaches in the processing of low grade-complex ore (Ata et al., 2001). Due to weathering and supergene enrichment of many copper deposits, these orebodies are typically (metallurgically) characterised by an oxidised zone, a transitional supergene zone and a hypogene sulfide zone as the deposit gets deeper. While the sulfide forms of copper (e.g. chalcopyrite, chalcocite, covelite) are easily upgraded through flotation, the oxidised overburden and transition zones may lead to significant copper losses due to poor floatability (Cropp et al., 2013). Often these weathered zones may also contain significant amounts of precious metals which are poorly recovered because of the high cyanide soluble copper loadings in alkaline cyanide leach circuits. Sulfuric acid is normally used to dissolve copper from the oxide/transition zone ores. However, sulfuric acid interacts with various altered and layer silicates, and oxide minerals to solubilise a range of metallic cations (K^+, Na^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}, Mn^{2+}), as well as anions such as halides (e.g. from atacamite). Many layer silicates tend to be gel-formers upon interaction with sulfuric and hydrochloric acid (formed from sulfuric acid in the presence of chloride bearing minerals or sea water). These silica gels, together with the accumulation of ions due to often prevalent water balance constraints, can cause severe operating challenges in solvent extraction circuits as well as heap leach environments where loss of permeability may result. The high ion loading may also lead to significant water treatment and neutralisation costs. Many copper minerals are inherently alkaline (oxides, carbonates, hydroxyl-halides and basic sulfates), as is the surrounding host rock of gangue minerals.

Sulfuric acid, which is the commonly employed lixiviant for leaching copper oxide ores has been observed to be infeasible for the leaching of ores containing high calcium-magnesium carbonate as gangue

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Table 1

The acid consumption and estimated time to complete the dissolution of common acid-consuming minerals in 10 g/L sulfuric acid solution (International Atomic Energy Agency, 2001).

Mineral		Specific acid consumption, kg/t		Time for complete dissolution
		1 day	250 days	
Albite	$NaAlSi_3O_8$	0.3	1.6	100–150 years
Microcline	$KAlSi_3O_8$	0.6	0.2	100–150 years
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)$	1.6	7.0	About 100 years
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	20.1	140.2	2–8 years
Vermiculite	$(Mg,Fe^{+2},Fe^{+3})_3[(Al,Si)_4O_{10}](OH)_2 \cdot H_2O$	39.3	247.2	2–8 years
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.6	23.7	30–50 years
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	15.7	64.2	10–20 years
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$	18.9	138.9	From 1 day to 7–8 years
Carbonized organics		33.6	60.5	Over 10 years
Pyrite	FeS_2	2.5	2.8	
Calcite	$CaCO_3$	930	998	1–10 days
Dolomite	$CaMg(CO_3)_2$	980	1065	Up to 10 days
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	940	1026	3–8 days
Siderite	$FeCO_3$	262	920	8–10 days
Magnesite	$MgCO_3$	114	1149	3–4 months
Limonite	$FeO(OH) \cdot nH_2O$			1–7 months

materials since these carbonates are very soluble in acids(Habashi, 1970; Pokrovsky et al., 2005; Vignes, 2013). The solubility reaction of calcium carbonate is shown in Eq. (1).

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \qquad (1)$$
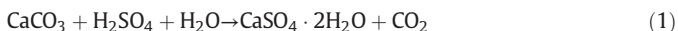
The dissolution of carbonate gangue minerals, which are often ubiquitous in copper deposits, leads to the consumption of large amounts of acid during the leaching of such ores, which can make the process uneconomical (Habashi, 1970, 1980; You-Cai et al., 2013). Table 1 shows the acid consumption and estimated time to complete the dissolution of major carbonaceous materials in 10 g/L sulfuric acid solutions. It can be seen that for acid leaching, each ton of carbonate mineral (e.g. dolomite, calcite, ankerite) requires about 1 ton of sulfuric acid.

The presence of calcium bearing carbonates during acid heap leaching processes also results in the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) which reduces heap permeability and solution percolation as was observed at the Twin Buttes mine in Arizona (Bartlett, 1998). In addition, the large quantities of gypsum may coat and passivate precious metals. Acid also reacts with sulfide minerals present in the supergene zone (e.g. chalcocite) to form elemental sulfur which is problematic when precious metals are present due to surface passivation. Also, a significant cyanide consumption may result from the reaction

of elemental sulfur with cyanide to form thiocyanate. Moreover, the formation of jarosites, which can lock up silver to form argentojarosites, may lead to significant precious metal losses, as well as toxic heavy metal inclusions that may be remobilised during weathering of such leach residues. In the recovery of valuable metals from deposits containing high acid consuming materials, an alkaline leaching medium presents many advantages over acidic medium, including increased selectivity, reduced corrosiveness and decreased reagent consumption. However, the conventional suite of alkaline lixiviants, such as cyanide and ammonia, is very limited particularly when reagent consumption is significant as for base metal ores. Both cyanide and ammonia share problems of toxicity, volatility, high lixiviant to base metal stoichiometric requirements, difficulties in recovery and recycle, and a tendency to oxidise.

Ammonia and its derivatives, such as ammonium hydroxide, are known to form very stable complexes with metal cations (cobalt, nickel and copper) through the nitrogen group and this has been observed to significantly enhance both the solubility and stability of the metals in solution (Greenberg, 1951). Leaching of malachite ore in aqueous ammonia/ammonium carbonate at 25 °C, solid to liquid ratio of 1:10, stirring speed of 300 rpm, particle size <450 μm, has been found to recover up to 98% of the copper in 120 min, while the gangue minerals did not dissolve in the solution (Bingöl et al., 2005). Other researchers (D'Aloya & Nikoloski, 2012; Liu et al., 2012; Oudenne & Olson, 1983; Wang et al., 2009; Yartaşi & Çopur, 1996) have also established that ammonia solutions are suitable for leaching carbonaceous copper ores. Despite the ammoniacal leaching medium having the advantage of selectively extracting copper, it has some technical and environmental challenges. Some of these challenges include its noxious odour detected even at low concentrations, its toxicity, and its adverse health effects such as burning of the respiratory tract and skin, the loss of reagent due to its volatility and the general difficulty in recovery and reuse. These challenges have limited the application of the ammoniacal system, especially in the economical heap leaching of low grade ores. According to the National Institute for Occupational Safety and Health (NIOSH, 1992), the threshold limit value for ammonia is 25 ppm for a normal 8 h shift. The ammonia-copper system also has a relatively
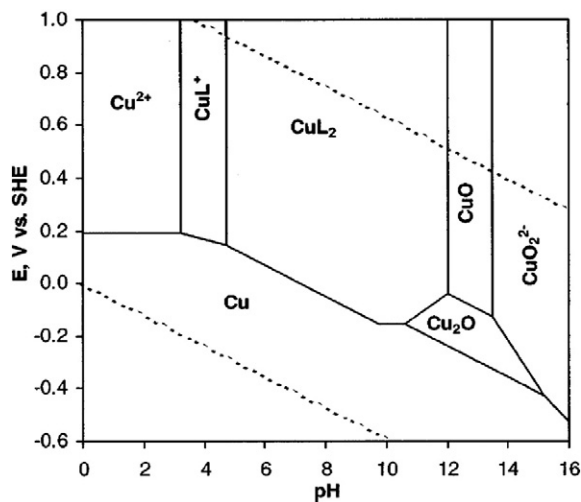

Fig. 1. Potential/pH diagram for the copper-water-glycine system for a total dissolved copper activity of 10^{-5} and a total glycine activity of 10^{-2} at 25 °C and 1 atm (Aksu and Doyle, 2002).

Table 2

Copper glycine complexes and their stability constants (Aksu and Doyle, 2001).

Copper Ion	Copper-glycine Complex	logK
Cu^{2+}	$Cu(H_2NCH_2COO)_2$	15.6
Cu^+	$Cu(H_2NCH_2COO)_2^-$	10.1
Cu^{2+}	$Cu(H_2NCH_2COO)^+$	8.6