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TECHNICAL COMMUNICATION

Copper Ion Recovery from Mine Water by Ion Flotation

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Abstract Solutions containing copper ions are produced at copper mines due to its dissolution from ores and dumps. It is important to recover these ions to prevent this toxic element from entering the environment and because it could be economical. We investigated the use of ion flotation for extracting Cu ions from diluted mine water from the Veshnaveh Mine in Qom, Iran. Experiments were conducted using floatation cells at pH 6, 9, and 12 with diluted solutions containing 10 mg L^{-1} of Cu. Sodium dodecyl sulfate and hexadecyl trimethyl ammonium bromide (HTAB) were used as collectors and methyl isobutyl carbinol (MIBC) and ethanol were used as frothers. The best result was achieved by maximizing Cu ion recovery and minimizing water recovery at pH 12, using 100 mg L^{-1} of HTAB and 0.1 % (v/v) of MIBC. Copper and water recovery were 79 and 24 %, respectively.

Keywords Metal leaching · Veshnaveh Mine · Qom

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Introduction

Copper is an important element for the growth of human tissues and bones. However, it is also a major water pollutants because of its aquatic toxicity, persistence, and stability. Consuming water containing concentrations of copper(II) above 1.3 mg L^{-1} in the short term causes gastrointestinal distress; long-term exposure can lead to liver and kidney damage (Bilal et al. 2013; US EPA 2009). In addition, excessive concentrations of this ion can be harmful to living creatures, soil, and plant species (Lamb et al. 2012).

Due to copper dissolution from ores and dumps, mine contact water can contain copper at concentrations that can be detrimental to the environment. Low concentration metal ions are often removed from water using methods such as chemical precipitation, ion exchange, electrolysis, and reverse osmosis. However, these methods are not economical for copper recovery because they require expensive equipment. In addition, they produce a large volume of secondary waste that requires disposal (Polat and Erdogan 2007) and the copper concentration in the solutions is so low that solvent extraction (SX) of copper cannot be used to recover the metal economically. These drawbacks have led to the development of a relatively new ion flotation method.

Ion flotation was initially introduced by Sebba (1959) as a method to recover metal ions from dilute aqueous solutions, yet it has hardly ever been used in environmental studies. It is based on the attraction of metal ions of opposite charge to the polar end of a surfactant molecule (collector) of opposite charge, the interaction of the hydrocarbon chain of the surfactant to air bubbles entering the cell, and ultimately on conveying the complexed metal ion to the foam phase (Galvin et al. 1993). Compared to other common methods, ion flotation, with its high recovery and selective separation, is a fast and relatively economical method that can be used to recover most of the metals in the periodic table at low concentrations (10^5 to 10^{-1} M; Nikol et al. 1992; Salmani et al. 2013; Zouboulis and Matis 1987). We therefore investigated the use of ion flotation to extract and recover copper from a dilute solution.

Laboratory Work

Materials and Equipment

In all of the experiments, Denver flotation cell types with a tank capacity of 2 L were used for flotation. Skimming was conducted manually with a rubber blade. The copper concentration was measured using an atomic absorption spectrophotometer (AAS). Sodium dodecyl sulfate (SDS), with a formula of $C_{12}H_{25}NaO_4S$ and a molecular mass of 288.4 g mol^{-1}, and hexadecyl trimethyl ammonium bromide (HTAB), with a formula of $C_{19}H_{42}BrN$ and a molecular mass of 364.5 g mol^{-1}, were used as collectors ($ka = 0.0004$ L mol^{-1}). Methyl isobutyl carbinol (MIBC) and ethanol were used as flotation frothers. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were used to adjust the pH. All of these materials were from Merck Millipore. The water sample was obtained from the Veshnaveh Mine, a copper mine in the city of Qom, Iran. Table 1 summarizes its composition.

Methods

To carry out the experiments, the mine water was first diluted so that the Cu concentration was 10 mg L^{-1}. Distilled water was used to dilute the leaching solution. Table 2 summarizes the chemical characteristics of the solution after dilution.

Table 1 Measured concentration of elements in the mine water from Veshnaveh Mine, Qom, Iran

Element	Concentration (mg L^{-1})
Ag	0.207
Cd	1.080
Co	7.606
Cu	8980
Fe	14,740
Mg	4260
Mn	466
Ni	17.1
Pb	7.84
Zn	297
pH	2.7

Table 2 Measured concentration of elements in the mine water after dilution

Element	Concentration (mg L^{-1})
Ag	<0.1
Cd	<0.1
Co	<0.1
Cu	10
Fe	16.4
Mg	4.75
Mn	0.5
Ni	<0.1
Pb	<0.1
Zn	0.3
pH	4

Due to the high concentration of Fe in the mine water, and to prevent Fe ion flotation during Cu flotation, the pH of the solution was raised to 4.5 (Lazaridis et al. 2004). At this pH, Fe ions are precipitated as iron hydroxide and can be removed by filtration, while Cu ions remain soluble. Magnesium was also present at high concentrations and its potential effect on the process had to be considered. Other elements that could have interfered were present at negligible concentrations.

A rotor speed of 750 rpm was used in all of the flotation experiments. The solution was stirred for 2 min, and its pH was set at 4.5. At that point, the collector was added. The solution was then stirred for two more minutes, the frother was added, and it was stirred for two more minutes. Afterwards, an aeration tube was used to aerate the solution in a Denver cell, which can be customized manually. A rubber blade (which helped prevent sample loss) was used to skim the froth. Froth samples were collected for the first 2 min (0–2) from when aeration started, and then at 2–5, 5–10, and 10–20 min periods. Froth samples were put into separate containers to assess their Cu ion concentration, which was measured by AAS. Water recovery was also measured.

Results and Discussion

In ion flotation, it is the metal ions, not the solid minerals that float. The efficiency of the method is based on the ratio of metal ion recovery to water recovery (Lazaridis et al. 2004). The pH of the solution is very important. With respect to Cu(II) species in the Cu–H_2O system, up until pH 9, the dominant Cu species are $CuOH^+$ and Cu^{2+}. At pH values of 6–12, copper hydroxide species are formed, and above pH 10, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ are the dominant species (Doyle and Liu 2003). Depending on the cupric species, either an anionic collector (with a negative charge) or a cationic collector (with a positive charge) must be used for flotation. Therefore, in flotation experiments at pH 6 and 9, a sodium dodecyl sulfate (SDS) anionic collector was used, and at pH 12, the HTAB cationic collector was used to convey the inactive surface ions.

When a sufficient quantity of air bubbles is produced by the cell, the Cu ions attach to the polar portion of the collector, while the non-polar hydrocarbon chain of the collector associates with the air bubbles. As a result, the complexed Cu ions are conveyed to the foam phase and recovered there. In the experiments, which used a diluted leaching solution with a Cu concentration of 10 mg L^{-1}, the collector concentration was 100 mg L^{-1}, and frother concentration was 0.1 %. In all stages of the experiment, the pH of the solution was adjusted using sulfuric acid and sodium hydroxide to pH 6, 9, or 12 (Tables 3, 4, and 5).

The cumulative percent recovery of Cu and water in foam at the end of the experiments (20 min) was found to be 38.5 and 21.4, respectively; at pH = 6, 42.8 and 23.8 at pH = 9, and 79.0 and 24.3 at pH = 12 (Tables 3, 4, 5). The maximum Cu recovery occurred at pH = 12 with the use of the HTAB collector. In addition, as shown in Fig. 1, the highest ratio of Cu:water recovery occurred at pH = 12. In the next series of experiments, at pH 6, 9, and 12, all conditions were held fixed, but MIBC was replaced with ethanol as the frother (Fig. 2).

Figure 2 shows again that pH = 12 had the maximum copper recovery (71 %) and the maximum ratio of copper ion: water recovery. Comparison of Figs. 1 and 2 reveals that the results for ethanol were similar to those with MIBC; ethanol simply reduced Cu recovery slightly and increased water recovery. Assuming that the flotation formula follows first order kinetics, Fig. 3 shows the kinetics of ion flotation of Cu and water in the experiment with the highest Cu recovery (pH = 12).

Higher percent recovery values will result in higher −Ln (1 − R) values. The Cu flotation kinetics constant (0.075 per minute) was higher than the water kinetics constant (0.013 per minute), demonstrating that Cu ions are recovered faster than water (Fig. 2). As flotation time increased, Cu and water recoveries increased also (Fig. 4).

To calculate the optimum flotation time, and to obtain a product with the most difference between the two recoveries using a first-order kinetics model, the following equations can be used:

$$E = R_{Cu} - R_w = \left(1 - e^{-K_1 t}\right) - \left(1 - e^{-K_2 t}\right) = e^{-K_2 t} - e^{-K_1 t}$$
$$dE/_{dt} = 0 \tag{1}$$

$$T = \ln(K_1) - \ln(K_2)/_{(K_1 - K_2)} \tag{2}$$

where E stands for efficiency, t stands for flotation time, and K_1, K_2 stand for first-order kinetics model constants in Cu and water recoveries, respectively. At constant amounts of Cu and water, the optimal flotation time was found to be 28.5 min, during which Cu and water recoveries were 88 and 30 %, respectively.

Most solutions used in hydrometallurgy processes contain more than one metal ion. As a result, a mechanical understanding of the selectivity power of one ion over the other proves very beneficial in choosing appropriate collectors and providing optimum conditions for ion flotation. In general, with two ionic species of the same element with different amounts of charge, the ion with the higher capacity acts more selectively than the one with lower capacity. In contrast, the rules of selective power between ions with equal capacities are not well known (Doyle 2003). Using a model derived from Graham's equation, Doyle (2003) included terms related to the Gibbs free energy of absorption to improve prediction of the selective power of ions:

$$\Gamma_M = \delta C_b \exp[-\left(\Delta G_{electric} + \Delta G_{hydrophobic} + \Delta G_{chelation} + \Delta G_{dehydration}\right)/RT] \tag{3}$$

where Γ stands for selective power (for the intended ion M^{n+}, e.g. Mg^{2+}), and $\Delta G_{electric}$, $\Delta G_{hydrophobic}$, $\Delta G_{chelation}$, and $\Delta G_{dehydration}$ stand for electrical interaction, hydrophobicity, complex formation (chelation), and dehydration, respectively. Also, T, R, δ, and C_b stand for

Table 3 Recovery of copper ions and water from foam at pH = 6, using SDS as a collector

Flotation time (min)	Froth (ml) (volume of extracted foam)	R-water (%) (water recovery in foam)	R-water (cum %, (cumulative recovery in foam)	C_{Cu} (mg L^{-1}) (copper value in each skimmed sample)	R_{Cu} (%) (Ion recovery in foam)	RCu (cum %) (cumulative metal recovery in foam)
0–2	31	1.55	1.55	30	4.65	4.65
2–5	35	1.75	3.3	33	5.78	10.4
5–10	94	4.7	8	21	9.87	19.5
10–20	267	13.4	21.4	14	18.7	38.5

Table 4 Recovery of copper ions and water from foam at pH = 9, using SDS as a collector

Time (min)	Froth (ml)	R-water (%)	R-water (cum)	C_{Cu} (mg L^{-1})	R_{Cu} (%)	R_{Cu} (cum)
0–2	25	1.25	1.25	28.6	3.58	3.58
2–5	66	3.3	4.55	25	8.25	11.8
5–10	101	5.05	9.6	18.8	9.45	21.3
10–20	283	14.2	23.8	15.2	21.5	42.8

Table 5 Recovery of copper ions and water from froth at pH = 12, using HTAB as a collector

Time (min)	Froth (ml)	R-water (%)	R-water (cum)	C_{Cu} (mg L^{-1})	R_{Cu} (%)	R_{Cu} (cum)
0–2	10	0.5	0.5	40.06	2	2
2–5	60	3	3.5	63.3	19	21
5–10	265	7.5	11	39.3	29.5	50.5
10–20	150	13.3	24.3	21.5	28.5	79

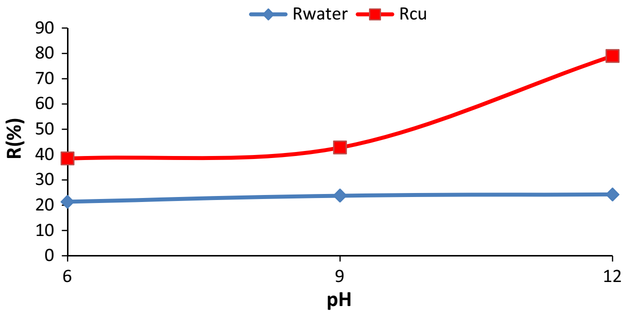

Fig. 1 Percent recovery (R) of copper and water at pH 6, 9, and 12 (MIBC frother)

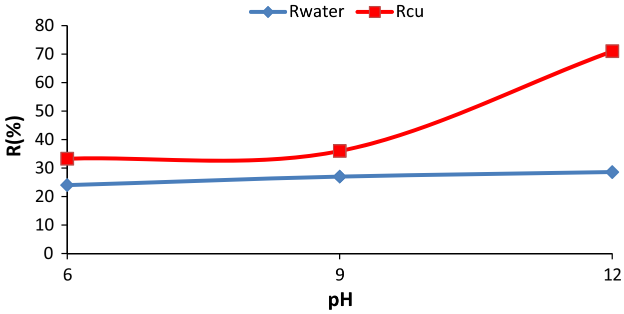

Fig. 2 Percent recovery (R) of copper and water at pH 6, 9, and 12 (ethanol frother)

temperature (in Kelvin), the universal gas constant, the thickness of different absorbed layers, and the metal ion concentration, respectively. Using this equation, a diagram was drawn by Doyle (2003) that compares the selectivity coefficients of various ions.

The Cu ion has greater selectivity than the Mg ion (Doyle 2003). Because the only ions present at appreciable concentrations in the Veshnaveh Mine water, after Fe is removed, are Cu and Mg (Table 2), Cu will be selectively removed relative to Mg.

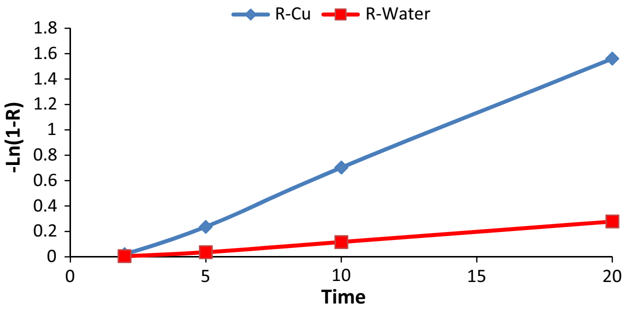

Fig. 3 Percent kinetics study of ion flotation of copper

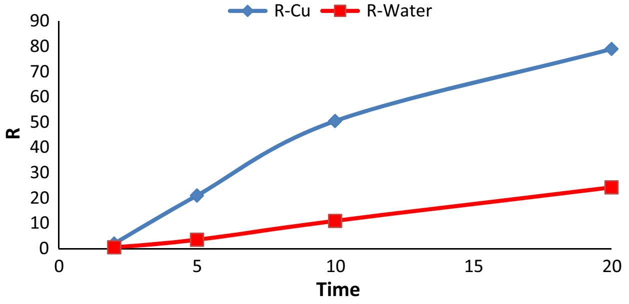

Fig. 4 Recovery of copper and water at pH 12 (considering first-order kinetics)

Conclusions

The feasibility of using ion flotation to recover Cu from a dilute leaching solution from the Veshnaveh Mine in Iran, with a total dissolved Cu concentration of 10 mg L^{-1}, was tested. Six sets of experiments with 36 samples were conducted using an anionic collector, SDS, at pH 6 and 9, and with a cationic collector, HTAB, at pH 12. MIBC and ethanol were used as flotation frothers. The highest Cu recovery (100 mg L^{-1}) occurred at pH 12 with HTAB, and MIBC; at 0.1 % v/v, Cu recovery was 79 % and water recovery was 24.3 %. In light of the results of these experiments at pH 12, and considering the fact that Cu was selectively recovered relative to Mg, it appears that Cu recovery can be successfully applied to these solutions using ion flotation to prevent or minimize environmental effects. Since these tests were performed in a laboratory environment, a field trial is warranted to assess the economics of this process.

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