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Abstract

Creatine was used as a lixiviant for gold dissolution from gold ore. The effects of creatine concentration, temperature, leach time, and pH were examined for their influence on extent of gold dissolution. The results show that at a temperature of 75°C and pH 11.5, gold dissolution increased from 51% to 88% on increasing creatine concentration from 25 to 50 g/t. Further increase in creatine concentration showed a negative effect on the gold dissolution. Gold dissolution increased from 47% to 87% by increasing the temperature from 25°C to 55°C, and from 61% to 89% by increasing pH from 10 to 11.5. Under the optimum conditions of solids' content of 30%, pH 11.5, creatine concentration of 100 g/t, temperature of 75°C, and hydrogen peroxide addition of 2%, about 90% of the gold could be dissolved from the ore after 24 h. A comparison between creatine and cyanide leaching showed that 90% gold dissolution was achieved at a cyanide concentration of 300 g/t, which is three times higher than the creatine concentration under optimal conditions.

Keywords

creatine, cyanide, gold dissolution, leaching

Introduction

Amino acids are organic compounds that are the building blocks of protein. They contain amino $(-NH_2)$ and carboxyl (-COOH) functional groups, along with a side chain (R group) that is specific to each amino acid. About five hundred naturally occurring amino acids are known. According to the number of amino and carboxyl groups, amino acids are classified into three groups: (1) neutral (one amino and one carboxyl), such as glycine, alanine, valine, leucine; (2) acidic (one amino and two carboxyl groups), such as aspartic acid, glutamic acid; and (3) basic (two amino and one carboxyl group), such as lysine and histidine (Nelson et al., 2005; Oraby and Eksteen, 2015a).

Geochemists have identified more than twenty kinds of amino acid in sediments and sedimentary rocks (Rashid and Leonard, 1973). They found that organic acids play an important role in the transport and concentration of gold in rock- and ore-forming processes.

Jingrong et al. (1996) studied the capability of organic acids (DL-aspartic amide, DL-alanine, glycine, L-galacystine, DL-aspartate, and histidine) to extract gold and identified suitable conditions. The study showed that gold is readily soluble in amino acids, with temperature, concentration, acidity, and type of amino acid being important factors affecting gold solubility. Using histidine, the highest solubility occurred at 80°C and at pH 6–8.

Leaching of gold from pure gold and gold ores in solutions of amino acid and cyanide solutions containing amino acids has recently been investigated (Azadi et al., 2019; Barani et al., 2021; Eksteen, 2014; Eksteen et al., 2017; Eksteen and Oraby, 2014, 2015; Oraby and Eksteen, 2014, 2015a, 2015b). Oraby and Eksteen (2014) investigated the selective leaching of copper from a gold–copper concentrate in glycine solutions. The results showed that 98% of total copper dissolved in a lixiviant system containing glycine and H_2O_2 , in 48 h at room temperature and a pH of 10.5–11. The copper dissolution rate increased with increasing glycine and H_2O_2 concentrations and increasing the pulp density decreased the copper dissolution rate. Oraby and Eksteen (2015a) also studied the leaching of gold, silver, and gold–silver alloys in glycine solution of glycine and H_2O_2 was capable of dissolving gold and silver. The gold dissolution rate increased temperature, glycine concentration, silver content, and pH. Eksteen and Oraby (2015) studied the leaching of gold from gold foils in the different amino acid solutions in the presence of hydrogen peroxide. The results showed that glycine ($C_2H_5NO_2$), histidine ($C_6H_9N_3O_2$), and

alanine (C₃H₇NO₂) dissolved gold even at low concentrations (0.1 M). The dissolution rate of gold increased with increasing amino acid concentration, peroxide concentration, and pH. Glycine dissolved more gold than histidine and alanine. Oraby et al. (2017) investigated the leaching of gold and copper from gold-copper ores and concentrates in cyanide and glycine-cyanide solutions. The results showed that the gold dissolution rate in the glycine-cyanide system was almost three times greater than that of conventional cyanidation. Oraby et al. (2020) also used glycine as a lixiviant in an alkaline environment for base and precious metals recovery from printed circuit boards. The results showed that in the first stage, alkaline glycine solutions selectively dissolved copper, zinc, and lead over precious metals; in the second stage, gold and silver were recovered using glycine and small amounts of cyanide. Barani et al. (2021) explored the leaching of a polymetal gold using cyanideglycine solutions. They found that at 75% of gold dissolved using 1500 mg/L cyanide (without glycine), 80% gold dissolution was achieved using 200 mg/L cyanide with 0.5 mg/L glycine, indicating a reduction in cyanide consumption of more than 80%.

In most previous studies, glycine is preferred over the other amino acids, because of its relatively low cost and bulk availability. In this study, creatine ($C_4H_9N_3O_2$) was used for gold recovery from a gold ore. To the authors' knowledge, creatine has not been reported as a lixivant for gold recovery.

Creatine is a popular sports supplement used to increase muscle mass, boost strength, and enhance exercise performance. It is a peptide. Peptides are generally formed when short chains known as peptide bonds form between two or more amino acids. The bonds, covalent in nature, form when the carboxyl group of one amino acid reacts with the amino group of another amino acid. Peptides can bond together, making long molecules known as polypeptides. The shortest polypeptides are dipeptides, which consist of two amino acids bonded by a single peptide bond. Creatine is formed from three amino acids: glycine, methionine, and arginine. Creatine supplements are available on the market in four forms: ethyl ester, gluconate, monohydrate, and nitrate (Stryer et al., 1995; Strumia et al., 2012). In this study, creatine monohydrate was used as a gold lixivant. Figure 1 shows chemical structure of creatine and creatine monohydrate.

Experimental procedure

Materials

The sample used in this research was taken from a run-of-mine (ROM) ore pile of the Agh-Darreh gold mine, which is one of two known gold deposits within the Cenozoic–Recent hydrothermal system of the Takab region in northwestern Iran. The host rock



Figure 1—Chemical structures of (a) creatine and (b) creatine monohydrate

of this deposit is mainly carbonate. Silver, mercury, iron, and manganese compounds occur in high amounts. The most important mineral containing gold in the sulfide zone of this deposit is pyrite (FeS₂). An ore sample weighing 40 kg was crushed and passed through a 270 μ m sieve. Sub-samples, each weighing 200 g, were prepared from the main sample by riffling. Figure 2 shows the particle size distribution of the representative sample. Table I shows the chemical compositions of the representative sample, determined by X-ray fluorescence spectroscopy (XRF; Philips X Unique II). The sample analysed mainly SiO₂, CaO, Al₂O₃, and Fe₂O₃. The gold content was determined by fire assay followed by atomic absorption spectrophotometry (AAS). The ore contained 2 ppm Au. X-ray diffractometry (XRD) showed, in order of abundance, that quartz, calcite, smectite, illite, dolomite, barite, goethite, kaolinite, iron arsenate dihydrate, jarosite, and pyrite occurred in the sample.

Mineralogy examination

A sample was divided into six size fractions (+50, -50+40, -40+30, -30+20, -20+10, and $-10 \ \mu m$); polished sections were prepared from each fraction. The sections were examined by scanning electron microscopy (SEM). Figure 3 shows backscattered-electron images. Image analysis showed that the gold particles were locked with other minerals in the coarse size fractions (+50 and $-50+40 \ \mu m$) (Figure 3-A). In the $-10 \ \mu m$ size fraction, gold particles were free—they were not locked with other minerals (Figure 3-B).

Leaching tests

The leaching tests were carried out in a stainless-steel laboratory reactor (1.2 L). The reactor was immersed in a water bath that controlled the temperature. In all experiments, analytical-grade reagents and deionized water were used. The ground ore sample (200 g) and 466 mL deionized water (30% solids by mass) were placed in the reactor. The pH was adjusted to the desired value by adding NaOH or H_2SO_4 . The desired amount of creatine was then added and the suspension was agitated (1000 rpm) for 24 h. Thereafter, the suspension was filtered and the Au in the dried cake and solution measured with AAS.

Results

Effect of creatine concentration

Figure 4 shows the effect of creatine concentration on the gold dissolution at solids' content of 30%, pH 11.5, 2% H₂O₂, temperature of 75°C, and leach time of 24 h. The gold dissolution increased from 51% to 88% with increasing creatine concentration from 25 to 50 g/t. Further increase in creatine concentration showed a negative effect on gold dissolution, decreasing from 89% to 84%



Figure 2—Particle size distribution of the sample



Figure 3-Backscattered-electron images of (A) -50+40 µm (arrow points to a locked particle of gold) and (B) -10 µm fractions (yellow particle is liberated gold)



Figure 4—Effect of creatine concentration on gold dissolution at leach conditions of 30% solids content, pH 11.5, 2% H₂O₂, leach time of 24 h, and temperature of 75°C

Table IChemical composition of representative sample	
Chemical species	Mass%
SiO ₂	49.59
CaO	11.52
Al ₂ O ₃	11.38
Fe ₂ O ₃	10.26
As ₂ O ₃	2.53
BaO	2.43
K ₂ O	1.81
SO ₃	1.8
MnO	1.61
PbO	0.745
ZnO	0.54
TiO ₂	0.41
Sb ₂ O ₃	0.3
Cl-	0.104
SrO	0.099
P_2O_5	0.01
MgO	0.01
LÕI*	4.85

*Loss on ignition

with increasing creatine concentration from 100 to 1000 g/t. As the creatine concentration increased beyond 100 g/t, the creatine molecules formed peptide bonds and the free creatine concentration decreased, which led to the decrease in the dissolution of gold.

Effect of temperature

Figure 5 shows the effect of temperature on gold dissolution at a creatine concentration of 100 g/t, solids content of 30%, 2% H_2O_2 , leach time of 24 h, and pH 11. The gold dissolution at



Figure 5—Effect of temperature on gold dissolution at leach conditions of 100 g/t creatine, 30% solids content, pH 11.5, 2% H₂O₂, and leach time of 24 h

room temperature (25°C) was low (47%), but increased to 87% on increasing the temperature to 55°C. Further increase in temperature to 65°C and 75°C had no significant effect on the dissolution of gold. The results show that temperature is an effective parameter in the range of 25–55°C.

Effect of pH

Figure 6 shows the effect of pH on gold dissolution at a creatine concentration of 100 g/t, solids content of 30%, 2% H_2O_2 , leach time of 24 h, and temperature of 55°C. The gold dissolution increased from 61% to 89% by increasing pH from 10 to 11.5. The gold dissolution decreased by about 6% points on increasing pH from 11.5 to 12. Gold dissolution in creatine-peroxide solutions is very sensitive to the leaching pH. Increasing the pH promotes



Figure 6—Effect of pH on gold dissolution at leach conditions of 100 g/t creatine, 30% solids content, 2% $\rm H_2O_2$, leach time of 24 h, and temperature of 55°C

decomposition of peroxide and generates hydroxide ions and oxygen (Equations [1] and [2]) or produces hydroxide radicals (Equation [3]) (Süss et al., 1998), which can accelerate gold dissolution (Nowicka et al., 2010). These results are consistent with those obtained for glycine (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015b).

$$H_2O_2 + OH^- \leftrightarrow H_2O + HOO^-$$
[1]

$$HOO^{-} + H_2O_2 \leftrightarrow H_2O + OH^{-} + O_2$$
 [2]

$$H_2O_2 \leftrightarrow 2\dot{OH}$$
 [3

Effect of leaching time

Figure 7 shows the effect of time on gold dissolution at a creatine concentration of 100 g/t, solids content of 30%, 2% H₂O₂, pH 11.5, and temperature of 55°C. Most of the gold (84%) dissolved in the first 12 h; dissolution only increased by a further 4% points from 12–24 h. Further increases in leach time to 32 and 48 h had no significant effect on gold dissolution. This can be explained by the reduction of gold concentration in solution and passivation of the gold surface by a layer of AuOH adsorbed to the gold surface (Oraby and Eksteen, 2015b). The dissolution also released sulfide ions, leading to the formation of a passive layer of Au₂S on the surface of gold, which reduces its dissolution (Dai and Jeffrey, 2006; Lorenzen and van Deventer, 1992).

Cyanide leaching

For comparison between creatine leaching and cyanide leaching, four leaching experiments at different cyanide concentrations were carried out at solids contents of 30%, pH 10.5, and room temperature. Figure 8 shows the percentage of gold dissolution after 24 h. The results show that the maximum gold dissolution (90%) was obtained at 300 g/t cyanide. This gold dissolution value (90%) was obtained by a 100 g/t cyanide solution.

Free cyanide in final filtrate solutions was immediately analysed by titration with AgNO₃ using rhodamine as colorimetric endpoint indicator (from yellow to salmon), following the routine recommended by the International Cyanide Code (2012), and described in the Standard Methods (APHA-AWW A-WEF, 1998). Figure 9 shows the free cyanide concentration in the final filtrate solutions. At a cyanide concentration of 300 g/t, 50% of the cyanide was consumed and 50% remained in the solution as free cyanide, which could be recycled or neutralized at a cost.



Figure 7—Effect of leaching time on gold dissolution at leach conditions of 100 g/t creatine, 30% solids content, 2% H_2O_2 , pH 11.5, and temperature of 55°C



Figure 8—Effect of cyanide concentration on gold dissolution at leach conditions of 30% solids, 2% H₂O₂, pH 11.5, and temperature of 25° C



Figure 9—Free cyanide concentration in cyanide leach solutions

Conclusion

Creatine was used as a lixiviant for gold dissolution from gold ore. The effects of creatine concentration, temperature, leach time, and pH were investigated for their influence on gold dissolution.

Gold dissolution increased from 51% to 88% with increasing creatine concentration from 25 to 50 g/t. Further increase in creatine concentration showed a negative effect. The results show that temperature is an effective parameter in the range of $25-55^{\circ}$ C. Gold dissolution increased from 47% to 87% with an increase in temperature from 25 to 55°C. Gold dissolution in creatine-H₂O₂ solutions is very sensitive to the leaching pH, increasing from 61% to 89% with increase in pH from 10 to 11.5. Most gold dissolved within 12 h, and longer leach times had no significant effect on the

dissolution. The optimum conditions were defined as solids content of 30%, pH 11.5, creatine concentration of 100 g/t, temperature of 75°C, and 2% H_2O_2 , at which almost 90% of the gold was dissolved from the ore within 24 h.

Using cyanide leaching, 90% gold dissolution was achieved at a cyanide concentration of 300 g/t and ambient temperature, which is three times higher than the creatine concentration under the optimal conditions. Approximately 50% of the cyanide remained in the solution as free cyanide, which can have safety, cost, and environmental consequences.

Bulk cyanide and creatine monohydrate prices are USD 1800–2200/t and USD 5000–10,000/t, respectively (Alibaba. com). Creatine monohydrate is 2.7–4.5 times more expensive than cyanide. To achieve a gold recovery of 90% from the investigated ore, cyanide consumption was almost three times that of creatine. However, leaching with creatine requires a higher temperature than cyanide, so its economic advantage remains unknown. A techno-economic study is required. As creatine is safer to work with and less harmful to the environment, we recommend that its application be explored further.

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