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Technical note

The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon

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article info abstract

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The leaching of gold and silver in a pH modified glycine solution in the presence of hydrogen peroxide was investigated. It was found that this lixiviant system can dissolve gold and/or silver under neutral and alkaline conditions at ambient to moderately elevated temperatures (23–60 °C). The gold leaching rate in solutions containing 0.5 M glycine and 1% peroxide at pH 11 after 48 h of leaching was found to be 0.322 μ mol/m² s, which is comparable to gold leaching rate after six days in thiosulphate–EDTA or thiosulphate–oxalate systems in the presence of thiourea (0.22–0.25 μ mol/m² s). In alkaline glycine–hydrogen peroxide solutions, it has been found that gold leach rate from gold–silver (50% Ag) alloy is about 6 times higher than rate from pure gold and the silver leach rate was 0.247 μ mol/m² s. An induction period of 48 h was noted for rolled precious metal foils, after which leaching rapidly accelerated. The reaction rate sensitivity to temperature can be explained by a mechanism that is chemical reaction controlling rather than mass transfer controlling as found for cyanide leaching. Precious metal dissolution rates increased with increased glycine concentration, increased silver content, and increasing pH (up to pH 11). The gold–glycinate complex was found to effectively load on activated carbon up to 13.2 g_{Au}/kg_{carbon} in 4 h.

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1. Introduction

Many different types of reagent suites have been investigated as potential alternative lixiviants for gold and/or silver. Thiosulphate, acidic thiocyanate, halides, thiourea and a range of more exotic organic reagents have been extensively tested [\(Pangum and Browner, 1996;](#page--1-0) [Jeffrey, 2001; Aylmore, 2005; Heath et al., 2008; Oraby et al., 2010;](#page--1-0) [Yang et al., 2011](#page--1-0)). However, the oxygenated alkali cyanide reagent suite remains the default choice for the industrial extraction of gold–silver ores. Most recently, thiosulphate based systems have been identified as potential industrial contenders to cyanide based systems [\(Choi et al., 2013](#page--1-0)). Yet thiosulphate lixiviant mixtures (e.g. copper ammoniacal ([Jeffrey et al., 2003; Senanayake, 2005\)](#page--1-0) or ferric-Tu–EDTA systems [\(Zhang et al., 2005; Heath et al., 2008\)](#page--1-0)) have many practical complexities and are often not environmentally benign. A calcium thiosulphate system has recently been commissioned by Barrick Goldstrike ([Choi et al., 2013](#page--1-0)) indicating some willingness to consider non-cyanide lixiviants for industrial niche applications, such as leaching gold from pregrobbing ores.

The main challenge in developing substitutes for cyanide is that the alternative for gold extraction should be inexpensive; less-toxic and effective to treat gold ore efficiently and economically when cyanide

Corresponding author. E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen). does not, or it should allow new resources to be processed which were previously uneconomic or not permitted.

In this exploratory research, glycine has been considered as a lixiviant for gold in an alkaline environment, with hydrogen peroxide as an oxidant. Glycine is the simplest α -amino acid with a carboxylic group and an amine group and is manufactured in bulk (in quantities similar in magnitude as cyanide) from acetic acid via chloro-acetic acid.

Amino acids are classified according to their acidity or the number of amino and carboxyl groups 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 acids, glutamic acid; (3) basic (two amino and one carboxyl group) such as lysine and histidine [\(Finar, 1963\)](#page--1-0).

Gold solubility in different amino acid solutions has been studied by [Zhang et al. \(1997\)](#page--1-0) who studied the environmental geochemistry of gold. Their results indicate that gold is soluble in amino acids and other organic acids and it is most soluble in the basic amino acids such as histidine. From a human health and biochemistry perspective, [Brown and Smith \(1982\)](#page--1-0) have examined the solubility of gold in solutions of different amino acids in skin secretions in order to assess the ability of these amino acids to dissolve gold and, hence, could be a possible source of allergic reactions in the human skin. Recently, [Feng](#page--1-0) [and Van Deventer \(2011\)](#page--1-0) have also found that gold extraction in thiosulphate solutions was largely improved by the addition of amino acids (L-valine, glycine, DL-alanine and L-histidine). It has also been noted ([Groudev et al., 1995\)](#page--1-0) that during the biological leaching of gold

Fig. 1. Effect of temperature on gold dissolution from a pure gold foil: 1 M glycine, 1% H₂O₂, pH 10, 350 rpm, at different temperatures.

from ores, the dissolution of gold was done by occurred via goldoxidising (peroxides) and a mixture of gold complexing (amino acids) agents secreted by the bacteria. Some of the identified micro-bacterial synthesised amino acids are asparagine, glycine, aspartic, histamine, serine and phenylamine and alanine [\(Korobushkina et al., 1974\)](#page--1-0). However, none of the authors performed a systematic kinetic study of gold and silver dissolution with single amino acids, or their pre-determined combinations, with suitable oxidants and pH ranges suitable for metallurgical extraction. Nor did any of the researcher's investigate any downstream concentration and recovery processes of gold glycinate and/or silver glycinate from their solutions.

The binding mechanism of gold in solutions containing amino acids involves initially the formation of a hydroxyl gold complex by an ionexchange mechanism. In alkaline solutions, gold is fixed by reduction of an intermediate species and chelating with gold bound to s-ligands [\(Bergeronm and Harrisony, 1989\)](#page--1-0). Many of the published data have focussed on studying the effect of organic matter on gold mobility, transport and chelating during the formation of lateritic gold deposits [\(Andrade et al., 1991; Colin and Vieillard, 1991; Zang and Fyfe, 1993;](#page--1-0) [Liu et al., 1994](#page--1-0)).

In alkaline pH, amino acids such as glycine, alanine, valine and phenylalanine complex gold where the amino acid coordination by the metal is effected through the amino and carboxyl groups. However, gold-amino acids bonds in histidine are coordinated through the nitrogen atoms of the amino group [\(Korobushkina et al., 1983\)](#page--1-0). The mechanism in which gold is combined with amino acid is mainly through coordination with atomic nitrogen in the amino group to form a covalent bonded complex and with oxygen in the carboxyl group to form ionic-bonded complex [\(Komnitsas, and Pooley, 1990; Jian and](#page--1-0) [Guifu, 1995\)](#page--1-0).

Glycine can exist in aqueous solutions in three different forms, namely $+H_3NCH_2COOH$ (cation), $+H_3NCH_2COO^-$ (zwitterion), and H₂NCH₂COO[−] (anion). It also forms a strong complex with gold(I) as $Au(H_2NCH_2COO)^{-2}$. The stability constant of gold with glycine at pH 9 is 18.0 which is higher than AuCl^{2−} (9.1), AuBr^{2−} (12.0) and $\text{Au}(\text{SCN})^{2-}$ (17.1) and $\text{Au}(\text{SO}_3)_2^{3-}$ (15.4), [\(Aylmore, 2005\)](#page--1-0). As an example, the stoichiometry of gold dissolution in alkaline glycine solutions is described in Eq. (1):

$$
2Au + 4(NH_2CH_2COOH) + 2OH^- + H_2O_2 \rightarrow 2Au(NH_2CH_2COO)_2^- + 4H_2O
$$
\n(1)

The processes of gold dissolution and precipitation depend on pH and E_h conditions of the medium and are more intensive in the presence of peroxides in alkaline media [\(Korobushkina et al., 1983\)](#page--1-0). [Brown](#page--1-0) [and Smith \(1982\)](#page--1-0) have found that the presence of hydrogen peroxide greatly enhances the gold and copper dissolution from gold jewellery dissolution.

To progress the understanding of alkaline glycine as a potential lixiviant, the effects of glycine concentration, hydrogen peroxide concentration, precious metal type and composition and temperature on the leaching, and the subsequent adsorption of the gold complexes on granular activated carbon, are evaluated below.

2. Experimental

2.1. Leaching

All experiments were carried out using solutions prepared from analytical grade reagents and Millipore water. Unless specified, all experiments are conducted using magnetic stirrers and Teflon coated magnetic stirrer bars. In a beaker, 400 mL of a solution containing 1 M glycine and 1% hydrogen peroxide was heated to 60 °C and stirred at 350 rpm. The evaporation effect during leaching at 60 °C was controlled by covering the leach beaker. The stirrer and beaker was also placed on an electronic balance to measure the difference of weight due to evaporation frequently during the experiment. Any decrease in the total weight was adjusted by adding distilled water to the leach solution. Rolled gold, silver and gold–silver alloy sheets (10 cm \times 1 cm \times 0.1 cm) were used in all the experiments and they were made from 99.99% pure gold and silver. Before each experiment, the surface of the each sheet was polished with Struers waterproof silicon carbide paper (FEPA P#2400). Finally, the gold sheet was washed with distilled water and allowed to dry in the presence of air at ambient temperature.

2.2. Adsorption onto activated carbon

To assess the use of activated carbon as a potential upgrading agent to adsorb the gold–glycinate complex, 1.5 g/L of fresh activated carbon was added into the pregnant solutions after leaching. The activated carbon used, had the following characteristics:

- Brand: PICAGOLD G210 AS,
- Size Range: $-2.36 + 2$ mm,
- Ash content of 2%,
- Density of 0.48 g/mL,
- Moisture content 2%

The carbon was washed and air dried at 65 °C prior to use. The adsorption experiments were conducted in 2.5 L Winchester bottles on a bottle roller at room temperature and rotation speed of 150 rpm. In order to evaluate the gold adsorption on carbon, sub-samples were taken at different time intervals and then diluted and stabilised with aqueous sodium cyanide before being analysed using ICP-OES.

Fig. 2. Arrhenius plot for the rate of gold dissolution as a function of temperature.

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