Spectroelectrochemical investigations of gold leaching in thiourea media

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Abstract

Surface-enhanced Raman scattering (SERS), facilitated via suitably prepared gold surfaces, has been used to observe sub-monolayer surface species and oxidation products derived from thiourea during leaching. Thiourea has been proposed as an alternative lixiviant to cyanide in gold extraction from ores, being particularly attractive for preg-robbing copper-containing ores. This investigation has shown that the C=S stretch band shifted to lower wavenumbers when adsorbed on the gold surface. Sorption of thiourea occurred concomitantly with co-adsorption of the electrolyte, whether chloride or sulfate. As oxidation continued, broad bands were observed at $\sim$330 cm^{-1} and $\sim$460 cm^{-1}, characteristic of v(Au–S) and v(S–S) modes, and indicative of the formation of a Au$_2$S-like phase. Formamidine disulfide, which has been purported to possess catalytic properties in the Au–TU leaching system, was not observed at the Au electrode. At high potentials a CN-containing species was observed at the electrode.
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1. Introduction

The development of non-cyanide lixiviants for gold leaching is of increasing interest to the mining industry, as political and public pressure mounts to find a cost-effective and safe cyanide-alternative. Proposed alternative lixiviants include thiourea (TU), halogens, thiocyanate, thiosulfate, ammonium polysulfide, malononitrile and cyanamide (McNulty, 2001). Thiosulfate has been considered a promising alternative, but has yet to find commercial application due to complex chemistry, passivation issues and recovery problems (McNulty, 2001). Acid–thiourea leaching of gold has been considered as a viable alternative to cyanide for some time (Groenewald, 1976; Li and Miller, 2006; Plaksin and Kozhukhova, 1941) and has been applied commercially to refractory aurostibnite concentrate at the New England Antimony Mine.

The perceived benefits of using a cyanide-alternative to leach gold include environmental, public health and handling advantages, in addition to application to refractory systems. An appropriate oxidant is required in TU leaching systems, with ferric sulfate shown to be the most effective (Li and Miller, 2006). Li and Miller (2006) cite studies that demonstrate that the initial rate of gold leaching with high concentrations of TU is comparable to cyanide leaching (Chen et al., 1980). However, reagent consumption (via thermal degradation, side-reactions, etc.) and passivation of the gold surface leads to relatively low extraction rates (Li and Miller, 2006). Other disadvantages of TU leaching include the need for tight controls on operating parameters and production of an acidic solution, requiring neutralization.

Thiourea is an organic compound which is soluble in water, and relatively stable in acidic solutions. Gold can be oxidised to an aqueous aurous TU species, as follows:

$$Au_{(s)} + 2C{=}S(NH_2)_{2(aq)} \rightarrow Au[C{=}S(NH_2)]_2^+ + e^- \qquad (1)$$
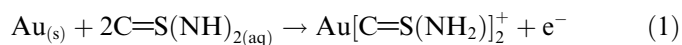
$E^0 = 0.380$ V (Kazakov et al., 1964), $\log(\beta) = 24$ (Puddephatt, 1987).

TU coordination to gold occurs through the sulfur atoms (Bolzan et al., 2003; Kania and Holze, 1998; Loo

et al., 2005; Piro et al., 2002). Auric ion (Au^{3+}) is unstable in TU solutions (Li and Miller, 2006). Kinetic comparisons have demonstrated that Au–TU leaching is faster in acid–sulfate systems, compared to acid–chloride or acid–nitrate electrolytes (Li and Miller, 2006), although some studies have demonstrated faster leaching in acid–chloride systems (Plaksin and Kozhukhova, 1941). TU is not stable under oxidizing conditions: strong oxidants (permanganate, dichromate, etc.) produce sulfate and ammonia, while moderate oxidants (ferric ion, peroxide, oxygen) produce elemental sulfur and urea, by way of formamidine disulfide (FDS, $[(NH_2)_2CSSC(NH_2)_2]$, $E^0 = 0.42$ V) (Li and Miller, 2006; Preisler and Berger, 1947). Electrochemical investigations have indicated that the electro-oxidation of TU on gold is quasi-reversible and occurs at $E > 0.3$ V(SHE), with highest Au dissolution efficiency therefore occurring below this potential (Bolzan et al., 2003; Groenewald, 1975). Ferric ion forms stable complexes with TU, and the rate of TU oxidation is believed to be relatively slow, such that gold–thiourea oxidation is favourable. Cupric ion has been shown to have a deleterious effect on gold–thiourea leaching and TU consumption.(Li and Miller, 2006).

Electrochemical investigations have proposed that gold–thiourea dissolution and TU electrooxidation occur concomitantly (Bolzan et al., 2003), while other reports suggest gold dissolution occurs well prior to TU oxidation (Shevtsova et al., 2006; Tian and Conway, 2004; Zhang et al., 2001). Zhang et al. (2001) noted that on the initial scan, the first anodic peak (which they attributed to Au dissolution) did not occur if the scan rate was rapid (0.1 V s^{-1}). They proposed that this might indicate that Au–TU dissolution results from a slow surface-step that is accelerated by FDS (Zhang et al., 2001). Shevtsova et al. (2006) proposed that the variable reports in the literature may be due to insufficient consideration of catalytic phenomena. They determined that a species produced at highly oxidizing potentials accelerated the dissolution of gold. However, they ascertained that FDS was not responsible for the observed acceleration (Shevtsova et al., 2006). Further investigation revealed that sulfide-ion, produced during TU oxidation processes, accelerated gold dissolution in TU solutions, and that the extent of acceleration relates to the sulfide coverage of the gold surface (Bek et al., 2005; Bek and Shuraeva, 2006). On the basis of these findings, passivation of the Au surfaces was further investigated and was explained in terms of "deactivation" of catalytically active adsorbed sulfide-ions (Bek et al., 2006).

In situ spectroscopic investigations of gold–thiourea leaching have been reported, using FTIRRAS (Bolzan et al., 2003). Bolzan et al. identified and assigned a band at 1434 cm^{-1} as relating to the formation of the soluble $[AuTU_2]^+$ complex in aqueous sulfuric acid. This band was attributed to $v(C–N) + v(C–S)$ modes and is blue-shifted ($\sim$30 cm^{-1}) from aqueous TU (Bolzan et al., 2003). The authors proposed that this related to an increase in the C–N and C–S stretching energies of the complex due to the greater double bond character of the C–N bond and

a decrease in the C–S bond order, consistent with a strongly polar sulfur–metal bond. FDS was observed as a band occurring at $\sim$1675 cm^{-1}, attributable to shifted δNH_2 modes, which accords well with other published studies (Bombicz et al., 2004; Yan et al., 1996). Surface passivation at high potentials was noted. Sulfur, as a TU oxidation byproduct, was not specifically observed.

More recently, gold leaching in alkaline TU solutions has been proposed (Chai and Wang, 2003; Wei et al., 1999; Zheng et al., 2006), with benefits cited as including less corrosive leaching solutions, improved leaching kinetics for gold and reduced leaching of associated minerals. In such systems FDS is the oxidant of choice and a TU "stabilizing" agent (such as Na_2SiO_3) is added. However, such systems are prone to complex chemistry, instability and reagent consumption.

The FTIR/Raman spectra of gold–thiourea compounds are not extensively reported (Bolzan et al., 2003). SERS is particularly suited to the *in situ* investigation of gold leaching, as water is a weak Raman scatterer. The submonolayer detection limits of the technique facilitate the observation of intermediates, oxidants and by-products at the electrode surface. This study reports a preliminary Raman investigation into gold dissolution in acidic TU solutions.

2. Experimental

Solutions were made with AR-grade chemicals and doubly de-ionized (DDI) reagent water (conductivity < 0.1 μS cm^{-1}). Glassware used in these experiments was cleaned in 7% HNO_3 (Analar) and rinsed repeatedly with DDI water. Thiourea stock solutions were made up immediately prior to each experiment. Reference compounds were synthesised in accord with methods described elsewhere (Bott et al., 1998; Piro et al., 2002; Preisler and Berger, 1947).

SERS spectroelectrochemical studies were conducted on a Renishaw system 100 using 632.8 nm excitation from a HeNe laser. The laser spot size was $\sim$50 μm with power at the sample measured as $\sim$6 mW (100% power). The scattered light was detected with a Peltier-cooled CCD detector with spectral resolution $\sim$2 cm^{-1}. The laser and scattered radiation were focused through an ultra-long working distance ×20 Olympus Plan Fl lens, NA 0.4. The spectra were not corrected for instrumental effects. The grating was calibrated using the 520.5 cm^{-1} silicon band. Some spectra of reference compounds were collected on a Renishaw InVia spectrometer, using 632.8 nm excitation.

Electrochemical experiments were conducted in a specially designed borosilicate electrochemical cell with an optically flat transparent window. A conventional three-electrode configuration was used, consisting of a platinum counter electrode, a Ag/AgCl/3.0 mol dm^{-3} KCl reference electrode and a gold working electrode. Potential control was maintained using an ADInstruments potentiostat controlled by a Maclab/4e analog–digital converter interfaced with a PC running ADInstruments EChem software. The cell was assembled with reference and counter electrodes