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Ion exchange adsorption and elution for recovering gold thiosulfate from leach solutions

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ABSTRACT

A new elution process for recovering gold thiosulfate from resins is described, and is based on the concept of synergistic ion exchange. In the presence of sulfite, $Au(S_2O_3)_2^{3-}$ is converted to $Au(S_2O_3)(SO_3)^{3-}$, which has a reduced affinity for strong anion exchange resins and is shown to be readily eluted by weaker eluants, such as chloride. Chloride has several advantages over other systems: it is significantly cheaper and more stable than trithionate, and the return of chloride loaded resin to the adsorption circuit is less problematic than nitrate. Using the proposed chloride + sulfite system, the majority of the gold is stripped within 2 BV of elution, and the gold can be readily recovered from the concentrated eluate using electrowinning. The copper is pre-eluted using ammonium thiosulfate, with stripping of 99.7% of the copper, and only 2.7% of the gold. The new elution process was operated in closed loop with a continuous 7 stage adsorption mini-rig, and a solution gold grade of <0.02 mg L^{-1} is obtained within 6 tanks. The composite solution tail over 24 h is 0.005 mg L^{-1} gold, indicating that the elution process produces a resin which is ideally suited for recycling without regeneration.

1. Introduction

Research into gold recovery using thiosulfate combined with resin in pulp (RIP) recovery has increased in recent years as it has the potential to be utilised for a number of niche applications. These include carbonaceous (preg-robbing) ores, and in locations where cyanidation is not possible due to political or environmental factors. The leaching of gold in thiosulfate solutions has been investigated extensively and is reasonably well understood (Muir and Aylmore, 2005), with thermodynamic studies indicating that $Au(S_2O_3)_2^{3-}$ is the predominant species formed during gold leaching in the thiosulfate–ammonia system (Senanayake et al., 2003). In the thiosulfate RIP process, the dissolved gold is then separated from the pulp through adsorption onto anion exchange resins. This process has been shown to be efficient, with good selectivity for the gold thiosulfate complex over other metal anions in solution (Nicol and O'Malley, 2002; O'Malley, 2002), however development of an appropriate elution technology to strip the gold from the resin once it has been adsorbed has proven more problematic.

Three main systems for the elution of gold thiosulfate from anion exchange resins have been previously proposed: thiocyanate, polythionates, and nitrate (Fleming et al., 2003; O'Malley, 2001). However none of these systems are ideal as:

- Thiocyanate elution is costly and also requires a complex regeneration procedure to recover the thiocyanate and recycle it.
- Concentrated trithionate solutions used in the polythionate elution system are unstable as they undergo hydrolysis, leading to loss of trithionate.
- Regeneration is required following trithionate elution, since the barren resin is completely loaded with trithionate, and its addition back to the adsorption circuit will reduce the gold loading.
- For the nitrate elution, the resin is returned to the adsorption circuit loaded with nitrate, leading to the accumulation of nitrate in the process water. This may ultimately impact on gold adsorption.

Other systems have also been proposed, including halides (such as chloride) and sulfite as eluants (Zhang and Dreisinger, 2003).

Each of these systems also requires a concentrated solution to effectively elute the gold as the gold thiosulfate complex has a strong affinity for the resin and requires a strong anion for effective exchange. Thus, research has focused on developing an elution technology based on the concept of synergistic ion exchange and is similar to the approach taken during the development of the so-called synergistic solvent extraction system for nickel/cobalt (Cheng, 2006). Given the success of this system and the similarities in the chemistry of ion exchange and solvent extraction, it is thought that the presence of an additive in the base eluant may alter the chemistry of the Au(I)–$S_2O_3^{2-}$ system and lead to a reduced affinity of the gold thiosulfate complex for the resin. This has the potential to result in more efficient elution of the gold and therefore lead to the adoption of lower concentrations of base eluant.

It has been reported previously (Perera et al., 2005) that the addition of sulfite ion to a solution containing $Au(S_2O_3)_2^{3-}$ results in

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the formation of two mixed thiosulfate–sulfite complexes, which exist in equilibrium with the gold thiosulfate complex (Eqs. (1) and (2)).

$$\mathrm{Au(S_2O_3)_2^{3-} + SO_3^{2-} \Leftrightarrow Au(S_2O_3)(SO_3)^{3-} + S_2O_3^{2-}} \quad K = 1.09 \pm 0.06 \tag{1}$$

$$\mathrm{Au(S_2O_3)_2^{3-} + 2SO_3^{2-} \Leftrightarrow Au(S_2O_3)(SO_3)_2^{5-} + S_2O_3^{2-}} \quad K = 4.8 \pm 0.3 \tag{2}$$

The investigation also found that $\mathrm{Au(S_2O_3)(SO_3)^{3-}}$ has an increased stability with respect to $\mathrm{Au(S_2O_3)_2^{3-}}$. Thus it is possible that a similar mixed thiosulfate–sulfite complex may form during gold thiosulfate elution using a sulfite containing eluant, thus changing the affinity of the complex for the resin, and leading to an enhanced elution of the gold (Jeffrey, 2007). The addition of sulfite to the eluant also has the potential to improve the quality of the product obtained from electrowinning, with mixed sulfite/thiosulfate baths shown to be very stable during the non-cyanide deposition of gold (Sullivan and Kohl, 1997).

2. Experimental

2.1. Apparatus

A Waters 2695 HPLC separation module was used for the analysis of all samples, with the separation being effected using a Dionex IonPac AS16 ion exchange column with 125 mM sodium perchlorate as the eluant (Jeffrey and Brunt, 2007). All analytes were detected using UV with a Waters 2998 Photodiode Array Detector. A pump flowrate of 1 mL min^{-1} was used, and the column temperature was 25 °C. Empower was the software used for the calculation of peak areas. All experiments were carried out using solutions prepared from either analytical grade or synthesized reagents and Millipore water. Sodium trithionate was prepared by the reaction of sodium thiosulfate and hydrogen peroxide, as outlined in the literature (Kelly and Wood, 1994).

2.2. Equilibrium gold thiosulfate loading

For the equilibrium loading experiments, 0.5 g of wet resin (Purolite A500/2788) was loaded for 5 h with 200 mL of solution containing 5 mM ammonium thiosulfate and 10 mg L^{-1} gold (as gold thiosulfate). Various sodium trithionate concentrations were investigated, in the absence and presence of 0.1 M sodium sulfite. After loading, the resin was filtered, washed and stripped with 2 × 50 mL of 0.5 M sodium perchlorate for 30 min. The resin was dried at 60 °C and then weighed. Barren and sodium perchlorate stripping samples were diluted with aqueous sodium cyanide (to stabilise the gold and copper) before being analysed using ICP-OES. Thiosulfate and polythionates were analysed by HPLC.

2.3. Batch gold loading and elution

For the initial elution experiments, 5 g of wet resin (Purolite A500/2788) was loaded overnight with 125 mL of a solution containing 100 mM ammonium thiosulfate, 100 mM ammonia, and 250 mg L^{-1} gold (as gold thiosulfate). Eluant was then pumped through an 8 mL column packed with the loaded resin at 5 BV h^{-1} (0.66 mL min^{-1}), with the fraction collector collecting 4 mL samples (0.5 BV). 50 samples (or 25 BV in total) were collected for each experiment, and samples were then diluted with aqueous sodium cyanide before being analysed using AAS.

2.4. Pre-elution of copper

For the copper pre-elution testwork, 6 g of wet resin (Purolite A500/2788) was loaded overnight with 4 L of a solution containing 25 mM ammonium thiosulfate, 1 mM sodium trithionate, 15 mg L^{-1} gold (as gold thiosulfate) and 20 mg L^{-1} copper (as copper sulfate), at pH 8.5. Eluant was then pumped through an 8 mL column packed with the loaded resin at 5 BV h^{-1} (0.66 mL min^{-1}), with the fraction collector collecting 8 mL samples (1 BV). 25 BV was collected for each experiment, and samples were then diluted with aqueous sodium cyanide before being analysed using AAS. Thiosulfate and polythionates were analysed using HPLC.

2.5. Electrowinning

The electrochemistry was conducted using a rotating disc electrode (RDE), and a rotation rate of 300 rpm was utilised. The potential or current was controlled using a PAR 362 potentiostat. A purposed built cell was used to electrowin gold from the eluate. This consisted of one cathode and two anode compartments, with a cell volume of 10 mL. 25 mL of solution was recirculated through the cell at 7 mL min^{-1}, and samples were withdrawn from the reservoir for gold analysis.

2.6. Continuous loading, elution and electrowinning

The loading of resin was conducted using a continuous mini-rig with seven stages of adsorption. Each adsorption stage contained 500 mL of solution, and 8 mL of wet resin (2.67 g of dry resin) which was contained in a cage that fitted neatly inside the reactor. The resin was suspended in the solution using an overhead stirrer with a twin blade paddle rotating at 150 rpm. The loading solution contained 25 mM ammonium thiosulfate, 0.37 mM sodium trithionate, 20 mg L^{-1} copper (as copper sulfate), and 1.15 mg L^{-1} gold (as gold thiosulfate) at pH 8. The solution flowrate was 4.17 mL min^{-1}, giving a solution residence time of 14 h (2 h per tank), and a maximum gold loading on the resin of 2475 mg kg^{-1} of dry resin. The resin was transferred counter-current 1 stage every 24 h, with the resin from stage 1 being eluted. Prior to elution, the resin was pre-eluted using 5 BV of 0.4 M ammonium thiosulfate, then washed with 2 BV of water, followed by the elution with 2 M sodium chloride and sodium sulfite. The resin was then washed with 2 BV of 1 M sodium sulfite and stored in water for ~16 h prior to being returned to stage 7 the following morning. Samples were diluted with aqueous sodium cyanide before being analysed using ICP-OES. Thiosulfate and polythionates were analysed using HPLC.

3. Results and discussions

This paper describes a number of individual research activities aimed at developing a new resin elution technology for the recovery of gold thiosulfate from leach solutions.

3.1. Gold thiosulfate equilibrium between solution and resin

The adsorption and elution of gold thiosulfate from strong base resins is an ion exchange mechanism, where there exists an equilibrium between the gold thiosulfate complex and a counter anion. It is known that trithionate competes strongly with adsorption of gold thiosulfate (Nicol and O'Malley, 2002), and also has been proposed as an eluant (Fleming et al., 2003), and therefore was chosen as the counter anion in experiments to determine the effect of sulfite on gold thiosulfate adsorption. The equilibrium, K, can be described as:

$$K = \left(\frac{Au{-}R}{Au{-}S}\right)^2 \times \left(\frac{Tri{-}S}{Tri{-}R}\right)^3 \tag{3}$$

where $Au\text{-}R$ and $Au\text{-}S$ are the equilibrium concentrations of gold on resin and in solution respectively, and $Tri\text{-}R$ and $Tri\text{-}S$ are the equilibrium concentrations of trithionate on resin and in solution