Recovering Gold from Thiosulfate Leach Pulps via Ion Exchange

Michael J. Nicol and Glen O'Malley

Increasing environmental and occupational safety concerns about the use of cyanide in gold processing has increased interest in more acceptable alternative lixiviants, the most promising of which is thiosulfate. However, the thiosulfate process lacks a proven in-pulp method of recovering the dissolved gold because activated carbon is not effective for the absorption of the gold-thiosulfate complex. This paper describes work aimed at evaluating the effectiveness of commercially available anion exchange resins for the recovery of gold from thiosulfate leach liquors and pulps.

INTRODUCTION

For more than a century, cyanidation has been the preferred method for extracting gold from ores. While cyanide can treat a wide variety of ore types, a growing number of so-called refractory gold ores are not readily amenable to cyanidation. In addition, pressure to ban or limit the operation of cyanidation plants is increasing due to a negative public perception about the environmental impact of the process. In order to overcome these problems, there has been an increase in research into alternate lixiviants for the leaching of gold from ores and concentrates. One of the most favored alternatives

to cyanide is thiosulfate, which is non-toxic, lower in unit cost in certain locations, and has the potential to leach gold more rapidly under suitable conditions. The recovery of gold may be higher from certain ores, such as those that contain large amounts of copper, other cyanide-consuming minerals, or carbonaceous materials.[1–5] However, the main limitations of thiosulfate leaching are the instability of thiosulfate, which leads to high reagent consumption, the complexity of its chemistry, and the lack of a viable in-pulp technique for recovering dissolved gold.[6]

This paper describes some of the work undertaken at the A.J. Parker Cooperative Research Centre for Hydrometallurgy, Australia's largest hydrometallurgical research organization. The objective of this research was to develop a resin-in-pulp process for recovering gold and silver from liquors and pulps produced in the leaching of gold ores and concentrates with thiosulfate as the lixiviant.

ADSORPTION OF GOLD

It has been found that strong-base resins are superior to weak-base resins because they have a greater capacity, which assists in reducing the competition from other anions within a leach solution. Some typical loading isotherms

for the gold-thiosulfate complex onto several commercial strong- and weak-base resins are shown in Figure 1. It is apparent that, in the absence of competing anions, gold loadings on strong-base resins of 60–90 g Au/L of wet-settled resin can be achieved at equilibrium concentrations in solution above approximately 5 mg/L of gold at a pH of 9.0.

In the case of weak-base resins, the achievable loading is considerably lower. This was also found to be the case for commercially available strong-base (Minix) and weak-base (Aurix) resins, which have shown some selectivity for gold adsorption from cyanide solutions.

Further studies with a selected commercial strong-base resin have shown that competing sulfur anions that are added to or formed during the leaching process can have a variable but significant effect on the equilibrium loading of gold. This is shown by the data in Figure 2, from which it is apparent that anions such as sulfate and thiosulfate do not have a major impact on the loading of gold but that sulfite and, to a greater extent trithionate and tetrathionate, are more strongly adsorbed and can thereby significantly suppress the adsorption of the gold thiosulfate complex. Thus, at a concentration of these species of 0.05 M in solution, the loading of gold is effectively reduced to zero. Tetrathionate is the primary product of the oxidation of the lixiviant, thiosulfate, by the copper(II) ammine, which is used as a redox mediator in the oxidation of gold.

$$2Cu(NH_3)_4^{2+} + 6S_2O_3^{2-}$$
$$\rightarrow 2Cu(S_2O_3)_2^{3-} + 8NH_3 + S_4O_6^{2-}$$
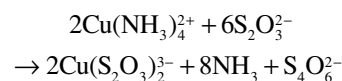
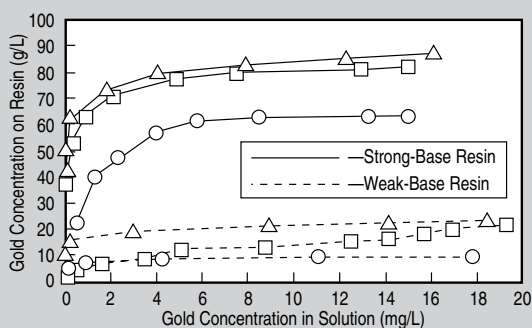However, tetrathionate is generally unstable at the pH values used in the

Figure 1. The equilibrium gold loadings onto strong-base and weak-base resins from a synthetic solution containing only the gold thiosulfate complex at pH 9.

Table I. Profiles Obtained in the Operation of the Mini-Plant on a Thiosulfate Leach Pulp+

	Gold			Copper	
	Solid (ppm)	Soln (ppm)	Resin (mg/L)	Soln (ppm)	Resin (mg/L)
Feed	4.2	8.9		8.7	
Stage 1	3.7	4.3	3,340	11.1	450
Stage 2		2.2	1,730	12.0	670
Stage 3		1.2	875	11.8	1,200
Stage 4		0.4	353	13.9	1,640
Stage 5		0.09	122	17.2	2,250
Stage 6	2.1	<0.05	26	17.3	4,580

leaching process and disproportionates to trithionate and thiosulfate.

$$2S_4O_6^{2-} + 3OH^- \rightarrow S_3O_6^{2-}$$
$$+ 5/2S_2O_3^{2-} + 3/2H_2O$$
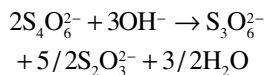
Kinetic experiments found that while the competing anions did not affect the initial rate of gold loading, it was important to minimize the contact time of the resin with the solution or pulp in order to minimize the displacement of loaded gold by competing anions over longer times.

Anionic metal thiosulfate complexes will also compete with gold for sites on the resin. The thiosulfate complexes of lead, zinc, copper, and silver may be found in a leach solution and are known to load onto anion exchange resins.[7] Figure 3 summarizes the effect of these base metals on the loading of gold onto the strong-base resin, Amberjet® 4200, from a synthetic thiosulfate leach solution containing 0.05 M thiosulfate, 0.2 M ammonia, and 20 mg/L of each of the metal ions.

The results show that
- The adsorption process is selective for gold over the other base metals, with lead being the only significant competing species.
- The adsorption of all metal ions varies with time of loading. A more extensive study of the kinetics has revealed that this is due to more rapid adsorption of the metal ion complexes compared to the competing sulfur anions and also to the increasing concentration of trithionate formed from the oxidation of thiosulfate at longer times. The less strongly adsorbed metal ion complexes are displaced by the trithionate ions. In the above experiment, the solution was found to contain 10 mM trithionate after 48 h.

The effect of the concentration of the competing anions on the loading of gold at the maximum point shown as occurring after about 300 min. in Figure 3 is shown in Figure 4.

The equilibrium-loading and kinetic studies have clearly demonstrated that efficient utilization of the capacity of the resins will depend greatly on the extent to which the concentrations of the strongly competing anions, tri- and tetrathionate, can be minimized in the leach solutions. This, in turn, will depend on the rate of oxidation of thiosulfate during the leaching and adsorption processes. The kinetics of the copper-catalyzed oxidation of thiosulfate are complex[8], but all indications are that the rate of the reaction will be reduced at low concentrations of copper ions, thiosulfate ions, and dissolved oxygen but high concentrations of ammonia. The preferential loading of gold at short contact times of the resin with the

solution will probably preclude the use of a resin-in-leach process.

CONTINUOUS RIP TESTWORK

A small-scale continuous resin-in-pulp (RIP) investigation was carried out in a laboratory mini-rig consisting of six 2.4 L mechanically agitated contactors. A peristaltic pump delivered the leached pulp at a flow rate of 3.4 L/min. to the first stage and, thereafter, the pulp flowed by gravity through the remaining stages. The resin, which was screened to provide beads greater than 0.6 mm, was manually transferred countercurrent to the pulp flow every 2 h for a period of 24 h in order to attain steady state. The resin was retained within each contactor by a screen with an aperture of 0.45 mm. The ore used in these experiments was leached for 24 h with 0.05 M thiosulfate, 0.8 M ammonia, and 1.0 mM sulfite at pH 9.5. The ore was a blend of a calcine from Kanowna Belle Gold Mine and an oxide ore from Boddington Gold Mine (both plants are in Western Australia) to obtain a gold concentration in the ore of 19 g/t. Before leaching, the pulp was screened to less than 180 μm and the pulp density was set at 40% solids.

The results obtained during a typical campaign with the mini-plant are given in Table I.
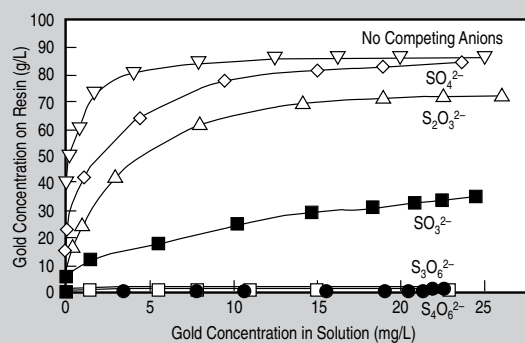
The results of these continuous runs

Figure 2. The effect of various sulfur species at a concentration of 0.05 M on the equilibrium gold loading onto a strong-base resin (Amberjet® 4200).
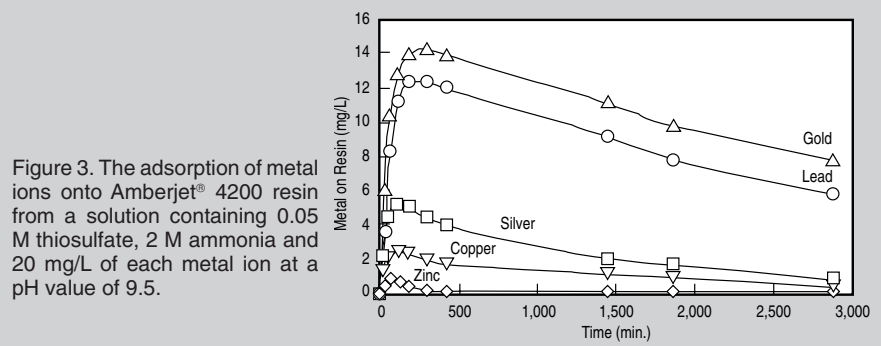
Figure 3. The adsorption of metal ions onto Amberjet® 4200 resin from a solution containing 0.05 M thiosulfate, 2 M ammonia and 20 mg/L of each metal ion at a pH value of 9.5.

showed that gold can be recovered from a leach pulp by a strong-base resin to yield gold loadings of 3,000 mg/L, barren pulp containing less than 0.05 mg/L of dissolved gold, and copper loadings of 500 mg/L. The leach pulp was found to contain 20 mg/L each of tri- and tetrathionate ions and the presence of these species limited the loading of gold that could be achieved. Loaded copper was displaced by gold, and at a loading of 2,000 mg/L gold, the copper loading was minimal at less than 500 mg/L. The resin was found to recover gold adsorbed on the solids that would otherwise have reported to tails if a solid/liquid separation method were used. This can be seen from the reduction in the gold content of the solids in passage through the RIP plant; an additional 10% recovery that would be lost if gold was to be recovered from the solution phase after solid-liquid separation.

ELUTION OF GOLD

Reagents that have been previously reported as effective for the elution of the metal thiosulfate complexes from strong-base resins are thiocyanate and
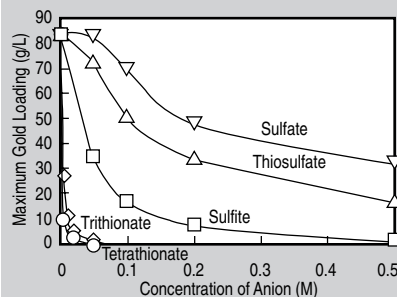
Figure 4. The effect of the concentration of competing anions on the maximum loading of gold from a solution containing 10 mg/L of gold thiosulfate and 2 M ammonia at pH 9.5.
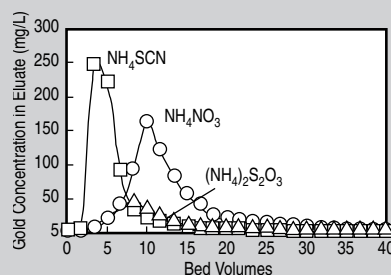
Figure 5. The solution profiles for the elution of gold thiosulfate from a loaded strong-base resin at a flow rate of 5 bed volumes/h with various eluants.
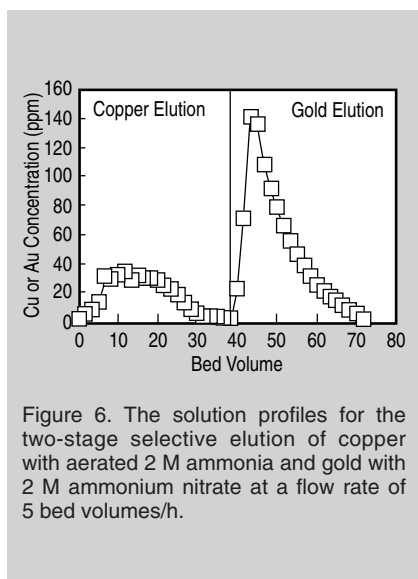
Figure 6. The solution profiles for the two-stage selective elution of copper with aerated 2 M ammonia and gold with 2 M ammonium nitrate at a flow rate of 5 bed volumes/h.

thiosulfate.[5] Figure 5 summarizes the results of a column elution of a loaded resin by the above eluants together with the results for elution with nitrate ions. While both nitrate and thiocyanate are very effective eluants for the gold thiosulfate complex with over 90% of the gold recovered with 30 bed volumes of eluant, only 30% of the loaded gold is eluted by thiosulfate.

The effectiveness of nitrate as an eluant was confirmed by studies of the equilibrium adsorption of gold thiosulfate in solutions of increasing concentration of nitrate (as ammonium nitrate). The results have shown that, for example, the equilibrium loading of gold in a 2 M ammonium nitrate solution containing 200 mg/L gold is 1 g gold/L of resin.

In order to minimize the cost of the copper and contamination of the gold product, it would be beneficial to recycle the loaded copper to the leaching circuit. It has been found that the loaded copper (I) thiosulfate complex can be relatively easily selectively eluted by conversion to the copper(II) amine.

Figure 6 presents profiles for the separate elution of copper and gold from the strong-base resin that was loaded during a countercurrent absorption run on the mini-plant. Thus, a two-stage elution process using oxygenated ammonia solution followed by an ammonium nitrate elution can be used to selectively and efficiently recover both the loaded copper and gold. It should be noted that if silver is also loaded onto the resin, results show that about 30% of the loaded silver would also be displaced with the copper from the resin.

CONCLUSION

Strong-base resins are the preferred choice for gold recovery because they have a higher gold loading capacity than weak-base resins. In particular, the strong-base resin Amberjet® 4200 exhibited good selectivity for the gold thiosulfate complex over other metal anions in solution. Small-scale counter-current absorption runs in a six-stage mini-plant with the strong-base resin achieved satisfactory gold loading and acceptable barrens.

References

1. D.S. Flett, R. Derry, and J.C. Wilson, "Chemical Study of Thiosulfate Leaching of Silver Sulfide," *Transactions of the Institute of Mining and Metallurgy. Section C: Mineral Processing and Extractive Metallurgy*, C92 (1983), pp. C216–223.
2. A.R. Marchbank et al., "Gold Recovery from Refractory Carbonaceous Ores by Pressure Oxidation and Thiosulfate Leaching," U.S. patent 5,536,297 (15 February 1995).
3. R.Y. Wan and K.M. LeVier, "Research and Development Activities for the Recovery of Gold from Non Cyanide Solutions" (Paper presented at the SME Conference, Salt Lake City, Utah, July 28 1993), pp. 415–436.
4. R.M.G.S. Berzowsky and V.B. Sefton, "Recovery of Gold and Silver from Oxidation Leach Residues by Ammoniacal Thiosulfate Leaching," presented at the 108th AIME Annual Meeting, New Orleans, Louisiana, February 18–22, 1979, pp. 1–17.
5. K.G. Thomas et al., "Gold Recovery from Refractory Carbonaceous Ores by Pressure Oxidation, Thiosulfate Leaching and Resin-in-pulp," U.S. patent 5,536,297 (2 February 1995).
6. N.P. Gallagher et al., "Affinity of Activated Carbon Towards Some Gold Complexes," *Hydrometallurgy,* 25 (1990), pp. 305–316.
7. L.C.T. Eusebius et al., "Thiosulfate as a Complexing Agent in the Separation of Cations by Anion-Exchange Chromatography," *Analyst,* 105 (1980), pp. 52–59.
8. J.J. Byerley, S.A. Fouda, and G.L. Rempel, "Kinetics and Mechanism of the Oxidation of Thiosulfate Ions by Copper(II) Ions in Aqueous Ammonia Solution," J.C.S. Dalton (1973), pp. 889–893.

Michael J. Nicol and Glen O'Malley are with A.J. Parker Cooperative Research Center for Hydro-metallurgy, Murdoch University, Perth, Western Australia.

For more information contact Michael J. Nicol, Murdoch University, Extractive Metallurgy Department, Murdoch, 6150 Western Australia, Australia; e-mail nicol@murdoch.edu.au.