

# RECENT ADVANCES IN THE DEVELOPMENT OF AN ALTERNATIVE TO THE CYANIDATION PROCESS - BASED ON THIOSULPHATE LEACHING AND RESIN IN PULP

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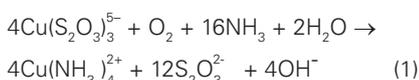
## ABSTRACT

A process based on thiosulphate leaching, followed by resin-in-pulp gold extraction, has been developed to treat the carbonaceous, preg-robbing ores of Barrick's Goldstrike orebody in the Carlin Trend of Nevada, USA. These ores have proven to be amenable to thiosulphate leaching, under mild conditions; gold leaches rapidly as the gold thiosulphate complex, which, because of its low affinity for graphitic carbon, does not suffer the preg-robbing phenomenon that is a feature of these orebodies in cyanide leach circuits. The mild leaching conditions are also compatible with a gold recovery process involving direct recovery from the leach pulp by adsorption on strong-base anion exchange resin. Finally, a novel elution/regeneration process has been developed to elute the gold off the resin, recover the gold from the eluate and restore the resin for recycling to the adsorption circuit.

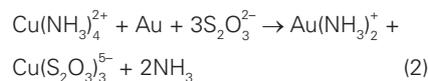
## INTRODUCTION

Thiosulphate leaching of gold (and silver) ores has been studied by many researchers over the years and there is an extensive literature on the subject. Some recent examples are the papers by Tozawa et al., 1981, Langhans et al., 1992 and Li et al., 1995. The chemistry is complex, involving thiosulphate, ammonium and copper ions, with oxygen as the oxidant. Many mechanistic schemes are possible, and no attempt will be made to present them all here. It seems that the copper ions act as an oxidation catalyst (because oxygen on its own generates slow kinetics) and that ammonium ions are important to maintain copper in solution at alkaline pH. To complicate matters, both ammonium and thiosulphate ions can complex with either gold or copper, with amine complexes being thermodynamically favored at higher pH values (>9) and thiosulphate complexes at lower pH values. One possible mechanistic scheme is described in the following equation:

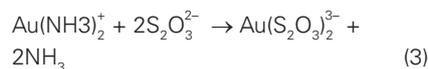
Oxygen reduction/copper oxidation



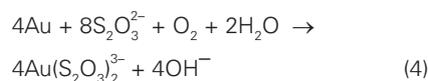
Gold leaching to form the gold-ammonia complex



Conversion from the gold-ammonia complex to old-thiosulphate complex



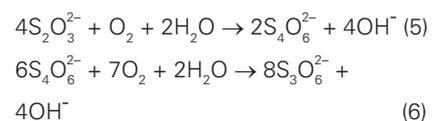
Overall reaction



The copper and ammonia are simply added as catalysts and are not consumed during the leaching of gold in the above scheme.

Thiosulphate is thermodynamically unstable in water, and is partially oxidized during leaching, to form polythionates such as tetrathionate and trithionate, as well as sulphate. The order of increasing

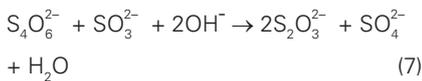
oxidation state is  $\text{S}_2\text{O}_3^{2-} < \text{S}_4\text{O}_6^{2-} < \text{S}_3\text{O}_6^{2-} < \text{SO}_4^{2-}$ . Sulphate is the most stable form of thiosalt and its formation is irreversible, whilst thiosulphate and trithionate are metastable in the presence of oxygen in aqueous solutions ( $\text{S}_2\text{O}_3^{2-} > \text{S}_3\text{O}_6^{2-}$ ), and tetrathionate is quite unstable ( $\text{S}_3\text{O}_6^{2-} \gg \text{S}_4\text{O}_6^{2-}$ ). The reactions for tetrathionate and trithionate formation are the following:



These reactions are undesirable for two reasons. Firstly, they contribute to loss of reagent, which must be compensated by fresh thiosulphate make-up. Secondly, both these anions load strongly onto anion exchange resins, as will be shown below, and their presence in the leach liquor reduces the loading of gold thiosulphate on the resin in an integrated thiosulphate leach/resin in pulp process.

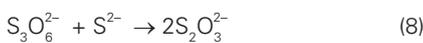
In fact, it is believed that the main reason for the success in developing an integrated thiosulphate leaching/resin in pulp process for Barrick's Goldstrike ores is the relatively low concentration of tri and tetrathionate anions produced during leaching. This in turn was probably a result of the mild leaching conditions needed for effective gold dissolution in this case (low thiosulphate, copper and ammonia concentrations, neutral pH and short reaction time).

To minimize reagent loss via the oxidation of thiosulphate, the leach liquor can be treated with sulphite, sulphide or hydroxide ions, after leaching is complete. Sulphite reduces tetrathionate back to thiosulphate (and is itself oxidized to sulphate), as follows:

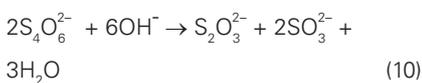


Trithionate anions are quite stable in the presence of sulphite.

Sulphide ions reduce both trithionate and tetrathionate back to thiosulphate as follows:



Increasing the pH of the leach liquor to >11 also results in a partial restoration of the thiosulphate concentration, due to hydrolysis of tetrathionate, which occurs under strongly alkaline conditions:



Trithionate is quite stable to alkaline hydrolysis.

Since leach liquors generally contain both trithionate and tetrathionate ions after a few hours of leaching, treatment with sulphide will generally be the most effective method of restoring the strength of the thiosulphate leach liquor. In addition, the sulphide ion is itself oxidized to thiosulphate in this process, so there will be a net gain in thiosulphate concentration, which will compensate for

losses due to complete and irreversible oxidation of thiosulphate to sulphate.

A word of warning relating to the use of sulphide to reduce polythionates back to thiosulphate! This reaction will also result in partial or complete precipitation of gold, so it can only be carried out after gold recovery. This is illustrated by the data in Table I, which were obtained by treating a thiosulphate leach liquor with sodium hydrogen sulphide. The intentions had been to reduce tetra and trithionate back to thiosulphate prior to gold recovery by resin in pulp. The results show that gold and copper thiosulphate precipitated from solution (presumably as sulphide complexes), before significant reduction of tetra and trithionate occurred.

The thiosulphate leaching process is not as universally applicable as the cyanidation process, because the gold thiosulphate complex,  $Au(S_2O_3)_2^{3-}$  ( $\beta_2 = 5 \times 10^{28}$ ) is somewhat weaker than the gold cyanide complex,  $Au(CN)_2^-$  ( $\beta_2 = 2 \times 10^{38}$ ). Consequently, gold recovery by thiosulphate leaching is usually slightly less efficient than can be achieved with cyanide, and higher concentrations of the lixiviant are needed to produce comparable leach kinetics.

One of the situations where thiosulphate leaching yields higher gold recovery than cyanide is the treatment of preg-robbing ores. This is a consequence of the low affinity of the gold thiosulphate complex for adsorption on carbon (Hemmati et al., 1989; Gallagher et al., 1990). This unique chemistry has led to the development of two patented processes for the

treatment of carbonaceous ores from the Carlin area of Nevada (Wan et al., 1994; Marchbank et al., 1996).

The most important negative consequence of the fact that the gold thiosulphate complex does not load onto carbon, is that the well-established processes of carbon in pulp (CIP) and carbon in leach (CIL) cannot be used for final gold recovery.

One alternative is to use cementation, as in the Merrill Crowe process, and this is the approach that has been adopted by Wan et al. (1993, 1994). They used cementation on copper powder rather than the more common zinc powder, because the copper cations that are released into solution during the gold reduction reaction are one of the ingredients of the thiosulphate leaching process. Since their process was being applied to a heap leach liquor, there was little incentive to develop an in-pulp treatment process.

However, Barrick were looking for a process to treat slurry from their pressure leaching operations at the Goldstrike Mine, and needed an 'in pulp' treatment process. Laboratory and pilot plant work carried out at SGS Lakefield from 1995 to 1998 led to the development of an effective, efficient, resin in pulp process, using commercial strong-base resins (Thomas et al., 1998). When coupled with thiosulphate leaching, the resin in pulp (RIP) flowsheet proved to be a technically viable, robust process, with capital and operating costs that compared favourably with the current Goldstrike operations (treating

NaSH	NH <sub>4</sub> OH	PH	Au mg/L	Cu mg/L	S <sub>2</sub> O <sub>3</sub> g/L	S <sub>3</sub> O <sub>6</sub> g/L	S <sub>4</sub> O <sub>6</sub> g/L
ADD'N	ADD'N						
% <sup>†</sup>	g/L*						
0	0	8.1	122	440	4.99	2.56	2.79
50	1.40	8.0	58.8	57.3	7.63	2.50	1.26
75	1.82	8.0	36.9	34.1	8.57	2.07	0.34
100	2.20	8.0	2.0	0.9	10.3	1.25	<0.1
†% relative to stoichiometric NaSH addition is based on equations 8 and 9.							
* Ammonia was added to maintain the starting pH.							

Table I. Reduction of Tetra and Trithionate, as well as Precipitation of Gold and Copper, by Treatment of a Thiosulphate Leach Liquor with Sodium Hydrogen Sulphide. (The thiosulphate leach liquor was spiked with commercial gold thiosulphate and copper thiosulphate reagents to increase their concentrations relative to the thiosalts, prior to addition of NaSH).

non preg-robbing ore) of autoclaving and cyanidation/CIL (see footnote).<sup>1</sup>

This paper describes the thiosulphate leach/RIP process developed for Goldstrike Mine.

## RESULTS AND DISCUSSION

### LEACHING/RESIN LOADING

Initial testwork involved small scale, rolling bottle or stirred tank experiments in the laboratory, in which the thiosulphate leaching conditions were optimized and minimized. A number of samples from different zones of the Goldstrike Mine were examined. The samples were all 'double refractory' in nature, containing gold locked up in sulphides as well as variable concentrations of preg-robbing graphitic carbon. These samples were representative of future Goldstrike reserves, and contrast the current feed material, which is generally sulphidic but not preg-robbing, and oxidized in autoclaves to achieve satisfactory gold recovery.

In all cases, the ore samples were first pressure leached using standard Goldstrike autoclave conditions (225°C, 100 psi oxygen partial pressure, 1 hour residence time) to oxidize the sulphides prior to thiosulphate leaching. Samples containing high carbonate concentrations relative to sulphide were pressure oxidized under alkaline conditions, while low carbonate ores were oxidized by Goldstrike's normal acidic autoclave process. This pretreatment released the gold from the sulphide matrix within which it was imbedded, and exposed it to the thiosulphate leach liquor.

After pressure leaching, the samples were cooled to about 60°C, neutralized with lime (where necessary), and then subjected to thiosulphate leaching. The following leaching conditions were established as 'standard' in the laboratory testing program, and were subsequently

proven to be adequate in several pilot plant programs.

Thiosulphate Conc = 0.05 M (5-6 g/L)  
Copper Conc =  $5 \times 10^{-4}$  M (20-50 mg/L)  
Ammonia Conc = 0.1 M (2 g/L)  
pH = 7.5 – 8.0  
Temperature = 40 – 60°C  
Leaching/Resin Loading Time = 8 hours

A comparison of gold recoveries achieved in batch tests with the thiosulphate/RIP process versus cyanidation/CIL, for several preg-robbing ores from Goldstrike Mine, is shown in Table II. The Screamer ore was subjected to alkaline pressure leaching, while all the other ores were pretreated by acidic pressure leaching prior to gold leaching. Identical splits of pressure leached ore were then subjected to the two gold leaching processes. The cyanidation/CIL results are all based on a standard procedure developed by Barrick, which simulates the recovery achieved in the full-scale cyanidation/CIL plant at Goldstrike.

Some of the samples displayed fairly weak pregrobbing tendencies, and hence achieved reasonable recoveries by cyanidation, but in all cases the thiosulphate/RIP process achieved superior gold recovery compared to the present cyanidation/CIL flowsheet at Goldstrike.

The thiosulphate/RIP process was tested extensively at SGS Lakefield in 1996-1997, both at bench scale and in several pilot plant campaigns, and was shown to be efficient, practical and chemically robust. Most of the testwork was done on a bulk sample of ore from the Screamer deposit, which was first pressure

leached under natural (weakly alkaline) pH conditions, in Lakefield's continuous autoclave, and then processed directly in a multi-stage thiosulphate leach, RIP circuit. In addition, several pilot plant campaigns were conducted on oxidized, non preg-robbing pulp, which was being produced at that time in the full-scale autoclaves at Goldstrike. This acidic pulp was first neutralized to ~pH 8, then preerated to oxidize any residual ferrous ion in solution, and finally treated through the same multi-stage thiosulphate leach/RIP pilot plant.

This pilot plant was operated in several 7-10 day campaigns, at a continuous pulp flowrate of 6-10 L/h and intermittent transfer of resin (usually once per shift) in a countercurrent direction. The loaded resin was eluted and regenerated on a daily basis and recycled to the last stage of RIP.

The resin used in this testwork was A-500C, a macroporous, large bead (95% >850 m), strong-base resin made by Purolite. The thiosulphate salt used in most of the laboratory and pilot plant work was ammonium thiosulphate (ATS) as this reagent provided two of the required ingredients. It was established in small scale testwork that the amount of ammonia/ammonium present in ATS (2 moles per mole thiosulphate) was sufficient for fast leaching kinetics, and no advantage was gained by adding supplemental ammonium sulphate.

The kinetics of gold leaching and resin loading were found to be fast, and the circuit was typically set up with 1 or 2 leaching stages (2 to 4 hours total residence time), followed by 4 to 6 RIP adsorption stages, each with a pulp

SAMPLE DESCRIPTION	HEAD GRADE G/T	GOLD EXTRACTION %	
		CYANIDE/CIL	THIOSULPHATE/RIP
Rodeo	9.1	78.5	87.6
Outpost	6.3	73.4	85.7
West Betze	7.2	88.2	92.2
North Betze	6.7	61.8	89.5
NE Deep Outpost	5.6	60.4	80.8
Screamer	6.2	40.3	84.6
Average	6.9	67.1	86.7

Table II. Gold Recovery by Cyanidation/CIL versus Thiosulphate/RIP for Several Goldstrike Ores

<sup>1</sup> Barrick conducted parallel testwork during 1997, 1998 on an alternative process for Goldstrike's preg-robbing ores, which involved whole ore oxygen roasting followed by cyanidation and CIL. This flowsheet also produced excellent metallurgical results with robust economics, and was ultimately selected by Barrick because of the lower technical risk. The Goldstrike roaster was commissioned in early 2000.

residence time of 1 hour.

A detailed analysis of all the pilot plant campaigns is beyond the scope of this paper, which seeks to present a summary of the overall process. Typical results from one of the campaigns are presented in Table III.

Gold loading on the resin was typically in the 2000 to 3000 g/t range, although loadings of over 5000 g/t were demonstrated.

Gold extraction from solution was generally very efficient, and barren solution values of 0.01 mg/L and less were routinely achieved.

It was observed in all the pilot plant campaigns that an additional 0.1 to 0.3 g/t gold was leached from the ore during RIP. This gold could not be leached by simply extending the leaching time, indicating that even the gold thiosulphate complex is weakly adsorbed on strongly preg-robbing ores. Thus, a resin-in-pulp process would be expected to achieve slightly higher gold recovery than a process involving solid-liquid separation after thiosulphate leaching.

Copper is present in the leach liquor, both as a cationic copper(II) amine

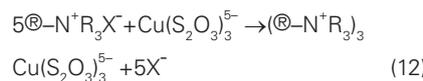
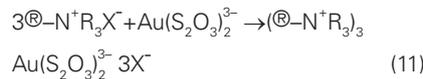
Conditions: Thiosulphate conc 5 g/L (as ATS), copper conc = 25 mg/L, pH = 8, temperature = 60°C.

SAMPLE DESCRIPTION	GOLD CONC			COPPER CONC	
	WASHED SOLIDS g/t	LEACH SOL'N mg/L	RESIN g/t	LEACH SOL'N mg/L	RESIN kg/t
Autoclave discharge	6.38				
Leach discharge	1.73	1.80		22	
RIP 1 discharge	1.54	0.49	2430	20	15.0
RIP 2 discharge	1.47	0.15	1375	20	15.2
RIP 3 discharge	1.44	0.06	729	22	15.5
RIP 4 discharge	1.42	0.04	421	22	14.9
RIP 5 discharge	1.38	0.02	195	15	12.3
RIP 6 discharge	1.37	0.01	88	5	4.5
Eluted resin			8		0.02
Extraction, %	78.5				
Copper eluate		4		2146	
Gold eluate		246		2	

Table III. Steady State Pilot Plant Profiles of Gold and Copper for a Pressure Leach/Thiosulphate Leach/RIP Process Treating Double Refractory Ore from the Screamer Zone of Barrick's Goldstrike Mine.

complex at higher pH values (>9) and an anionic copper(I) thiosulphate complex (equation 1) at lower pH values (<9). In the latter form, which would be expected to dominate under the Goldstrike leach conditions (~pH 8), it is co-extracted with gold thiosulphate by the anion exchange resin. Although strong-base resins have been shown to be quite selective for gold thiosulphate over copper thiosulphate, copper loadings of 10 to 20 kg/t on the resin were achieved in the Goldstrike pilot plant runs, and most of the copper was generally extracted from solutions.

The following equations describe the ion exchange equilibria for gold and copper loading as their thiosulphate complexes on strong-base resins



where the symbol ® refers to the resin matrix.

**ELUTION**

**Original Flowsheet:** Initial testwork focused on a 2-stage elution process. Copper thiosulphate is relatively weakly adsorbed on the resin and was shown to be efficiently eluted with a strong solution of thiosulphate, under ambient conditions. Gold elution with thiosulphate was insignificant. After most of the copper (>99.9%) had been eluted, gold was then eluted with a strong thiocyanate solution, also under ambient conditions, and at neutral pH.

It was established during the pilot plant campaign that the amount of thiosulphate needed to elute the copper from the resin (typically 4 bed volumes of 100-200 g/L ATS) was less than the amount of new ammonium thiosulphate make-up needed for leaching. When the process was operated as a split elution, with the first two bed volumes advancing to leach and the second two bed volumes being recycled as the first half of the next elution cycle, the composition of the advanced eluate was typically 2000-4000 mg/L copper, ~10 mg/L gold and 100-200 g/L ATS. Thus, the method developed provided not only an inexpensive means (zero reagent consumption) of selectively eluting copper from the resin ahead of gold elution, but also allowed the copper needed for the leaching process to be recycled internally.

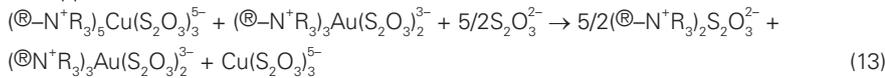
Gold elution with thiocyanate ions (typically 4-6 bed volumes of 50-100 g/L SCN-) was also very efficient. The concentration of gold on the resin was reduced from 2000-3000 g/t down to less than 10 g/t (>99.5% elution) under ambient conditions, in 2-4 hours.

This process also lent itself well to a split elution technique, with the first half of the eluate (2-3 BV at 250- 500 mg/L gold) reporting to gold recovery, and the second half (typically <10 mg/L gold) being recycled directly to elution as the first half of the next cycle.

Typical elution profiles for copper and gold from one of the pilot plant campaigns are shown in Table IV.

The equations describing the elution reactions are given below:

1) Copper Elution



2) Gold Elution



SAMPLE ANALYSED		COPPER (g/t,mg/L)	GOLD (g/t,mg/L)
Loaded Resin		19,200	2309
Copper Eluant	BV1	2120	~10
(~150 g/L S <sub>2</sub> O <sub>3</sub> )	BV2	4930	~10
	BV3	593	~10
	BV4	57	~10
Gold Eluant	BV1	<10	90
(~100 g/L SCN)	BV2	<10	560
	BV3	<10	45
	BV4	<10	5
	BV5	<10	2
	BV6	<10	1
Eluted Resin	g/t	<10	5
Elution Efficiency	%	99.9	99.8

Table IV. Elution of Copper with Thiosulphate and Gold with Thiocyanate from Strong Base Resin from the Barrick Thiosulphate/RIP Process. (Temperature ~20°C, Eluant flowrates 2 BV/h, Eluant pH 6-8 (natural)).

At the end of the gold elution step, all of the resin functional groups are occupied with thiocyanate ions, because of the high affinity of strong-base resins for this anion.

During the first pilot plant campaign, the resin was recycled directly to RIP, without regeneration to remove the thiocyanate. The pilot plant performed well during this period, with insignificant decrease in gold recovery due to the presence of thiocyanate on the recycled resin. This thiocyanate was displaced from the resin when the functional groups loaded up with copper and gold thiosulphate, and reported to the RIP tailings at a concentration of 150-200 mg/L SCN<sup>-</sup>.

Whilst the pilot plant performed well for the duration of the first campaign (~10 days), it was recognized that direct recycling of the resin in the thiocyanate form would probably be unacceptable, for the following reasons:

- the cost of the thiocyanate lost to the tailings was a significant percentage (~10%) of total operating costs;
- if tailings water was recycled to the leach process (which would be desirable to conserve thiosulphate and minimize effluent treatment costs), thiocyanate would accumulate in solution and reach a concentration where it would eventually have a negative effect on gold and copper loading in RIP;
- the presence of thiocyanate in the tailings was considered undesirable from a long-term environmental point of view.

For these reasons, initial research effort focussed on developing a regeneration process for treating the resin after gold elution, to strip off the thiocyanate, hopefully in a form that would allow it to be recycled within the gold elution process.

These attempts were only partially successful.

The first regenerant tested was sulphuric acid. Because of the low affinity of strong-base resins for HSO<sub>4</sub><sup>-</sup> compared to SCN<sup>-</sup> (K<sub>SCN/HSO4</sub> = 2700), it was necessary to use a large volume (up to 20 BV) of fairly concentrated sulphuric acid (~100 g/L) to displace 80-90% of the SCN from the resin. The process partially achieved its objective in that the concentration of SCN in the RIP tailings decreased almost tenfold, to 10-20mg/L, during the second pilot plant campaign, when sulphuric acid regeneration was incorporated in the flowsheet. However, it was not possible to recover the SCN from this regenerant solution in a useful form, so the process failed in its other objective of reducing operating costs. More serious, however, was the observation that the rate of resin breakdown in RIP increased quite significantly in the second pilot plant campaign. This was ascribed to the osmotic effect of going from neutral pH (loading and elution) to strongly acidic (regeneration) processes, which causes the resin to shrink and swell by up to 20% of its volume every cycle. In the first pilot plant campaign there was no regeneration, and the resin was in a neutral pH environment throughout its cycle. Resin losses were not quantified in these small-scale pilot plant campaigns, but a great many broken beads were observed in the fine screen at the RIP discharge during the second campaign, whereas no broken beads had been observed in the first campaign.

As a result of the resin breakage problem with sulphuric acid, an alternative thiocyanate regeneration process, which uses ferric ions to complex thiocyanate and remove it from the resin (Fleming, 1985) was never tested, as it was felt that this acidic process would also produce high resin losses.

The second regenerant tested was a strong (neutral pH) ammonium thiosulphate (ATS) solution (300 g/L). Although strong-base resins are very selective for thiocyanate over thiosulphate, it was hoped that a strong thiosulphate solution would displace most of the SCN from the resin by mass action. The hope was to strip the SCN off the gold-eluted resin with strong thiosulphate solution, and then use the

same regenerant to elute the copper off the resin – in the first stage of the overall process. If the SCN stripped from the resin during final regeneration could subsequently be loaded onto the resin during copper elution, SCN would be conserved within the elution process, meeting both the economic and environmental requirements of the process. This conceptual flowsheet, which is shown schematically Figure 1, was incorporated into the third pilot plant campaign. The concentration of thiosulphate regenerant and the deportment of thiocyanate are also shown in the figure.

This process was elegant on paper, but failed to achieve the desired performance when it was tested in the third pilot plant campaign. The maximum amount of ATS available for regeneration was fixed by the ATS make-up requirement for the leaching process, and this maximum allowable quantity of ATS stripped only 25 to 40% of the SCN from the gold-eluted resin. The pilot plant performed well from a gold recovery perspective in the third campaign, but thiocyanate concentration in the RIP tailings was still >100 mg/L. The result achieved was an improvement on the flowsheet tested in the first pilot plant campaign (no regeneration), but failed to adequately address the economic and environmental concerns around high levels of thiocyanate in the RIP tailings.

**New Flowsheet:** Further research was initiated on the development of a new gold elution process; one that did not involve the use of thiocyanate for gold stripping. The development work focussed on the tetrathionate and trithionate anions.

Tetra and trithionate anions are known to load strongly on anion-exchange resins, competing effectively with the gold and copper thiosulphate complexes for resin functional groups. It was therefore reasoned that, if concentrated solutions of these anions could be produced, they would probably perform well as gold eluants.

Initially, research effort was focussed on developing methods of manufacturing tetra and/or trithionate solutions

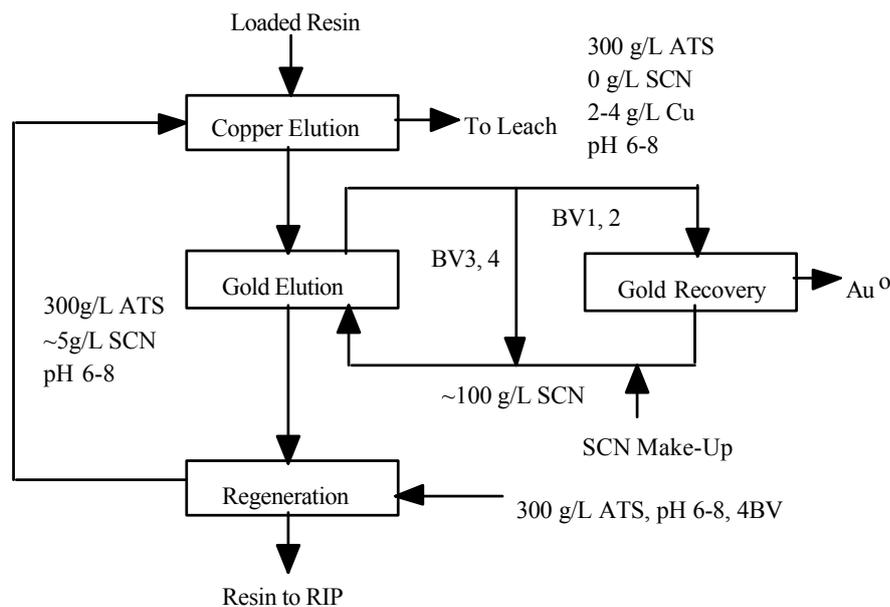


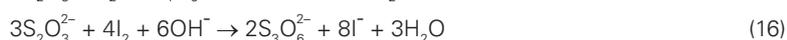
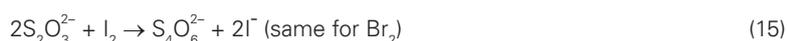
Figure 1. Flowsheet for the Elution of Loaded Resin from a Thiosulphate Leach/RIP Circuit, Involving Copper Elution with Thiosulphate Solution, Gold Elution with Thiocyanate Solution and Resin Regeneration with Thiosulphate Solution.

inexpensively. No suppliers of trithionate could be found amongst the chemical manufacturing companies, and tetrathionate, whilst available in small batches from several suppliers, was too expensive in this pure form to be considered for an industrial process.

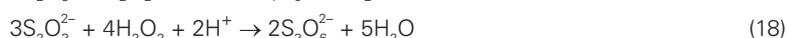
#### a) Synthesis of polythionates

The methods of synthesizing polythionates that were investigated in the laboratory involved oxidation of a concentrated thiosulphate solution, using oxidants such as halogens, hydrogen peroxide and sulphur dioxide. A lot of testwork was carried out, and the most important results are summarized in Table V.

The following reaction stoichiometries are proposed for these oxidation reactions:



(same for Br<sub>2</sub>)



The following conclusions can be drawn from the results in Table V.

- Oxidation of thiosulphate with iodine at natural (acidic) pH yields a solution containing predominantly tetrathionate, with lesser trithionate, and minimal formation of wasteful oxidation products, such as elemental sulphur and sulphate ions. Controlling the pH at ~8 during thiosulphate oxidation, by the addition of base, is not beneficial, because the yield of tetra and trithionate decreases due to the formation of S<sup>0</sup> and SO<sub>4</sub><sup>2-</sup>. The high cost of iodine makes this method of producing tetra and trithionate extremely expensive.
- Although bromine is much cheaper than iodine, this method also yields an unacceptably high cost of tetra and trithionate production, mainly due to the poor yields of the desired product. Oxidation with bromine (both at the natural, acidic pH

TEST NO.	OXIDANT	OXIDATION CONDITIONS	THIOSALT CONCENTRATION, g/L						FINAL pH	APPROX COST \$/kg*
			INITIAL S <sub>2</sub> O <sub>3</sub> <sup>†</sup>	FINAL S <sub>2</sub> O <sub>3</sub>	FINAL S <sub>4</sub> O <sub>6</sub>	FINAL S <sub>3</sub> O <sub>6</sub>	FINAL SO <sub>4</sub>	FINAL S <sup>0</sup>		
1	I <sub>2</sub>	100% stoich, nat pH	152	4	105	23	2	0	1.9	40-60
2	I <sub>2</sub>	100% stoich, cntrl pH	160	2	103	29	10	32	8.4	
3	Br <sub>2</sub>	100% stoich, nat pH	205	0	60	10	53	22	0.7	4-6
4	Br <sub>2</sub>	100% stoich, cntrl pH	124	48	25	15	20	11	6.3	
5	H <sub>2</sub> O <sub>2</sub>	100% stoich, nat pH	164	51	0	134	48	0	10	1.0-1.5
6	H <sub>2</sub> O <sub>2</sub>	100% stoich, cntrl pH	190	15	0	163	66	0	8	
7	H <sub>2</sub> O <sub>2</sub>	100% stoich, cntrl pH	123	39	0	109	30	0	6	
8	H <sub>2</sub> O <sub>2</sub>	100% stoich, cntrl pH	129	0	79	51	85	0	3	
9	H <sub>2</sub> O <sub>2</sub>	100% stoich, cntrl pH	241	0	57	34	198	67	2	
10	SO <sub>2</sub> /air	1.5gSO <sub>2</sub> /gS <sub>2</sub> O <sub>3</sub> nat pH	100	51	39	37	NA	0	2.1	
11	SO <sub>2</sub>	1.1gSO <sub>2</sub> /gS <sub>2</sub> O <sub>3</sub> nat pH	100	48	42	38	NA	0	1.6	0.5-1.0
12	SO <sub>2</sub>	3.1gSO <sub>2</sub> /gS <sub>2</sub> O <sub>3</sub> nat pH	200	36	101	159	13	0	0.9	
13	SO <sub>2</sub>	3.1gSO <sub>2</sub> /gS <sub>2</sub> O <sub>3</sub> cntrl pH	200	171	0	3	0	0	6.9	

†The initial thiosulphate concentrations are calculated values, after correction for increases in volume due to addition of aqueous oxidants.

\* The quoted costs are based on the reagent costs for the initial thiosulphate and oxidant only, per kilogram of combined thionate (S<sub>4</sub>O<sub>6</sub> + S<sub>3</sub>O<sub>6</sub>) produced. Other costs such as power and labour are assumed to be fairly insignificant, and similar for the different processes. reagent costs for the initial thiosulphate and oxidant only, per kilogram of combined thionate (S<sub>4</sub>O<sub>6</sub> + S<sub>3</sub>O<sub>6</sub>) produced. Other costs such as power and labour are assumed to be fairly insignificant, and similar for the different processes."

Table V. Production of Polythionate Solutions of Various Composition by Oxidation of Thiosulphate with Different Oxidants

and at a controlled, neutral pH), resulted in the formation of excessive amounts of elemental sulphur and sulphate.

- Peroxide is an efficient thiosulphate oxidant, and under both neutral pH (6-8) and natural pH (10-11) conditions, produces trithionate with no tetrathionate. When the pH is controlled in the acidic range (pH 5), a significant amount of tetrathionate is produced. Unfortunately, at least 10-20% of the thiosulphate is oxidized all the way through to sulphate, irrespective of the pH of the reaction

The cost of trithionate production by peroxide oxidation is reasonable, and this would be the chosen method if it was important to make a trithionate solution with no tetrathionate

- Oxidation with sulphur dioxide produces the best yields of thionate products, at the lowest cost, and would be the preferred method in most case. As can be seen from equations 19 and 20, the SO<sub>2</sub> used to oxidize thiosulphate is itself reduced to tetra and trithionate, so directly contributes to the yield of product.

The SO<sub>2</sub> oxidation method should be carried out at the natural, acidic pH that is produced by bubbling SO<sub>2</sub> gas through the thiosulphate solution. Attempting to control the pH at a neutral pH of 7 by addition of caustic suppresses the oxidation reaction.

Oxidation with SO<sub>2</sub> gas at the natural acidic pH apparently produces approximately equal concentrations of tetra and trithionate. If it is assumed that reactions 19 and 20 occur at the same rate, the sum of these two reactions yields the following stoichiometry:



On this basis, the stoichiometric amount of SO<sub>2</sub> would be 1.3 g SO<sub>2</sub>/g S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. However, the results in Table V show that only about 50% of the thiosulphate was oxidized after this amount of SO<sub>2</sub> had been added.

It is likely that some SO<sub>2</sub> was lost to the vapor phase in these tests, and that better utilization will be achieved with a well designed gas/liquid absorption reactor. Even at a SO<sub>2</sub> utilization of only 50%, the cost of polythionate production will be less than \$1/kg, and could be as low as 10c/kg, depending on the cost of SO<sub>2</sub> gas (which could be in the range from zero to ~50c/kg). Tetrathionate is relatively unstable in aqueous solution and oxidizes slowly to trithionate. The production of a mixture of tetrathionate and trithionate during the oxidation process is therefore not really a problem or an issue, as everything will end up as trithionate (plus sulphate) after a sufficient period of time, whichever oxidation method is chosen. Moreover, as shown below, both tetrathionate and trithionate (as well as a mixture of the two) are very effective as eluants for gold thiosulphate on strong-base resin.

**b) Elution of gold with trithionate anions** A concentrated trithionate solution was made by oxidizing a ~400 g/L thiosulphate (as ATS) solution with a 30% v/v solution of hydrogen peroxide. The natural pH of the reaction (~10) was reduced to pH 6-7 with sulphuric acid during addition of peroxide. The stoichiometric addition of peroxide (according to equation 18) resulted in the oxidation of 75% of the thiosulphate in the original solution. The inefficiency was due to the further oxidation of 20% of the thiosulphate through to sulphate. The elution tests were carried out with a resin that had been loaded from a synthetic gold thiosulphate/copper thiosulphate solution to similar concentrations as those achieved in the pilot plant. The results presented in Table VI show that a 200 g/L solution of trithionate elutes 99.8% of the gold from a strong-base resin with about 6 BV of eluant, in 3-4 hours, under ambient conditions. A split elution technique would produce a pregnant eluate contained 200-250 mg/L gold and <10 mg/L copper.

Temperature ~20°C, Eluant flowrate = 2BV/h, Eluant pH = 6-8 (natural)

SAMPLE ANALYSED		Au mg/L, g/t	Cu mg/L, g/t	S <sub>2</sub> O <sub>3</sub> mg/L, g/t	S <sub>3</sub> O <sub>6</sub> g/L	S <sub>4</sub> O <sub>6</sub> g/L	SO <sub>3</sub> g/L	SO <sub>4</sub> g/L
Loaded Resin		2911	24900					
Copper Eluant	BV1-4	1.6	2450	101				
(150 g/L S <sub>2</sub> O <sub>3</sub> )								
Gold Eluant	Feed			75	200	3.3	1.7	103
	BV1, 2	383	10.9	86	120	12.5	3.5	68
	BV3, 4	71	0.3	73	201	17.8	6.1	110
	BV5, 6	21	0.6	74	204	15.9	5.7	110
	BV7, 8	1.3	0.3	69	190	14.1	6.5	100
Eluted Resin		7.2	<50					
Elution Efficiency								
Gold Elution, %		1.0	99.9					
Gold Elution, %		98.8	<0.1					
Total, %		99.8	99.9					

Table VI. Elution of Copper with Thiosulphate and Gold with Trithionate from Strong Base Resin.

Temperature = 20°C, Eluant flowrate = 2 BV/h, Eluant pH ~1.5 (natural).

SAMPLE ANALYSED		Au mg/L, g/t	Cu mg/L, g/t	S <sub>2</sub> O <sub>3</sub> mg/L, g/t	S <sub>3</sub> O <sub>6</sub> g/L	S <sub>4</sub> O <sub>6</sub> g/L	SO <sub>3</sub> g/L
Sample Analysed		Au mg/L, g/t	Cu mg/L, g/t	S <sub>2</sub> O <sub>3</sub> g/L	S <sub>3</sub> O <sub>6</sub> g/L	S <sub>4</sub> O <sub>6</sub> g/L	SO <sub>3</sub> g/L
Loaded Resin		2955	23500				
Copper Eluant	BV1-4	1.12	2280	108			
Gold Eluant	Feed			0.13	43.5	79.8	<1
	BV1, 2	698	13.7	27.8	59.8	25.3	<1
	BV3, 4	55	3.7	<1	63.9	61.1	4.5
	BV5, 6	9.3	0.4	<1	61.9	49.9	4.4
	BV7, 8	5.1	0.4	<1	65.1	51.9	3.7
Eluted Resin		24	<10				
Elution Efficiency							
Gold Elution, %		0.3	96.9				
Gold Elution, %		99.1	3.1				
Total, %		99.4	99.9				

Table VII. Elution of Copper with Thiosulphate and Gold with a Mixed Polythionate Eluant, Containing Predominantly Tetrathionate and Lesser Trithionate Anions.

**c) Elution of gold with tetrathionate anions**

A concentrate solution of tetrathionate (plus trithionate) was prepared by oxidizing a 100 g/L solution of thiosulphate with sulphur dioxide. The final solution contained ~80 g/L tetra and ~40 g/L trithionate at its natural pH of ~1.5.

The copper and gold elution results are presented in Table VII, which show that tetrathionate is an even better eluant than trithionate for gold thiosulphate on a strongbase resin.

**d) Regeneration of resin after elution**

with trithionate and/or tetrathionate  
Regeneration of the eluted resin with sodium hydrogen sulphide (NaSH), as per equations 8 and 9, was tested by circulating a dilute solution (<2 g/L) of NaSH through a bed of eluted resin. The amounts of trithionate and tetrathionate on the resin were estimated by analyzing the eluted resin for total sulphur, and assuming that all of the resin functional groups were occupied by S<sub>3</sub>O<sub>6</sub><sup>2-</sup> or S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, in equal proportion.

The eluted resin contained 21.8% S (dry mass basis), equivalent to 87 g/L on a wet volume basis. This is equivalent to a calculated trithionate concentration of 0.45 moles/L (0.9 equivalents/L) on the resin, and tetrathionate of 0.34 moles/L (0.68 equivalents/L). The total capacity of the resin, calculated on this basis (1.58 equivalents/L) is slightly higher than the published capacity of strongbase resins (1.2 – 1.5 equivalents/L).

The effect of sulphide regeneration was assessed by treating three resin samples from the same batch of eluted resin. One sample was a control, which was contacted with 10 BV of water in a bottle on a roller overnight. The second sample was treated with 10 BV of solution containing 0.7 g/L sulphide as the sodium salt. This provided 70% of the required sulphide to complete the conversion of tri and tetrathionate on the resin, according to equations 8 and 9. The third resin sample was treated with a solution containing 1.25 g/L sulphide, which provided 120% of the stoichiometric amount of sulphide. In each case, there was <0.01 g/L sulphide and ~12 g/L thiosulphate left in solution

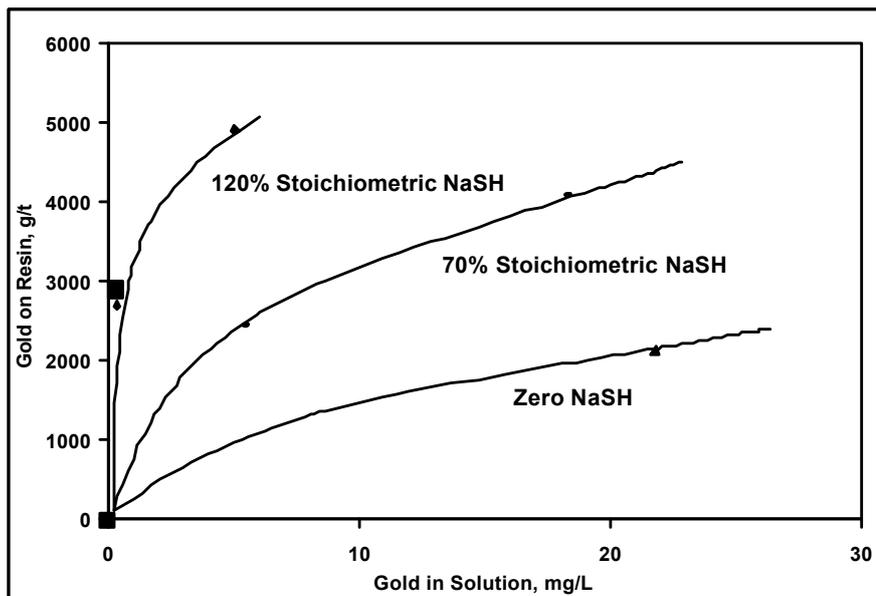


Figure 2 – The Equilibrium Loading of Gold Thiosulphate on a Strong-Base Resin Before and After Regeneration with Sodium Hydrogen Sulphide, (the equilibrium point denoted ■ refers to fresh resin).

after treatment, indicating complete reaction of the sulphide with the polythionate species in the resin matrix.

After regeneration, the three resin samples were contacted with a synthetic gold thiosulphate solution to determine the effect of regeneration on the capacity of the resins for the gold thiosulphate complex. The results are shown in Figure 2, and indicate that sulphide is very effective at restoring the capacity of the strong-base resin.

**e) Recovery of gold from polythionate eluates**

Cementation with iron or copper powder has been investigated as methods of recovering gold from polythionate eluates. Both these reductants were effective for the treatment of gold thiocyanate eluates, but have proven to be less effective for the treatment of polythionate eluates

The results of a 4-cycle test, in which the same batch of trithionate eluate was used to elute four successive batches of loaded resin, are shown in Table VIII. The eluate was treated with iron or copper powder to cement out the gold after each elution cycle.

The results show that cementation with iron powder was reasonably efficient in the first cycle, although a large excess of iron was needed (~60 g Fe per gram of gold). However, the efficiency dropped from 94% in the first cycle to 56% in the second cycle, and the eluate had to be retreated with successive, high concentrations of iron and copper powder to reduce the gold in solution to <10 mg/L. In the two subsequent cycles (3 and 4) copper powder was used, and although it proved to be more effective than iron powder, a significant amount of the excess copper powder was leached into the trithionate eluate, and its presence seemed to have a serious

effect on gold elution efficiency.

Work is continuing in this area, and alternatives that are being tested include electrolysis, precipitation with sulphide and reduction with borohydride.

**f) Stability of polythionate eluates.**

A solution of trithionate (~150 g/L) was made up, and then split three ways. The sub-samples were kept in sealed bottles for 3 weeks and maintained at pH values of 6, 8 and 10 respectively. Samples were taken periodically and analysed for thiosalt speciation to determine the rate of break down of trithionate (Note: this is the species of particular interest, since tetrathionate breaks down relatively more rapidly, to form trithionate).

The results indicated that the half-life for trithionate break down (at all 3 pH values) was about 1 week. This is a fairly high rate of break down, which means that the most economical way of incorporating polythionate elution into an overall, integrated process may be to:

- synthesize polythionate on site by treatment of concentrated thiosulphate solution with SO<sub>2</sub> gas (equation 19)
- use the polythionate solution as the eluant for gold elution (equation 14)
- recover the gold by precipitation with sulphide, at the same time reducing the polythionate back to thiosulphate (Table 1, equations 8 and 9).
- use the barren eluate as a copper eluant and then as thiosulphate make-up in the leach circuit.

Conceptual flowsheets for this scheme are shown in Figures 3 and 4.

CYCLE NUMBER	GOLD ON RESIN			CEMENTATION		GOLD IN ELUATE			COPPER IN BARREN ELUATE
	LOADED g/t	ELUTED g/t	EFFICIENCY %	METAL POWDER	CONC g/L	PREG mg/L	BARREN mg/L	EFFICIENCY %	
1	2911	7	99.8	Fe	7.5	119	7	94	<1
2a	2758	11	99.7	Fe	7.5	121	53	56	2
2b				Fe	7.5	53	11	91	<1
2c				Cu	10	11	1	99	3200
3	2505	181	88.3	Cu	15	112	7	93	4800
4	2591	307	83.4	Cu	15	82	10	88	7580

Table VIII. Elution of Gold Thiosulphate with a 200 g/L Solution of Trithionate Followed by Cementation of the Eluted Gold and Recycle of the Barren Eluate

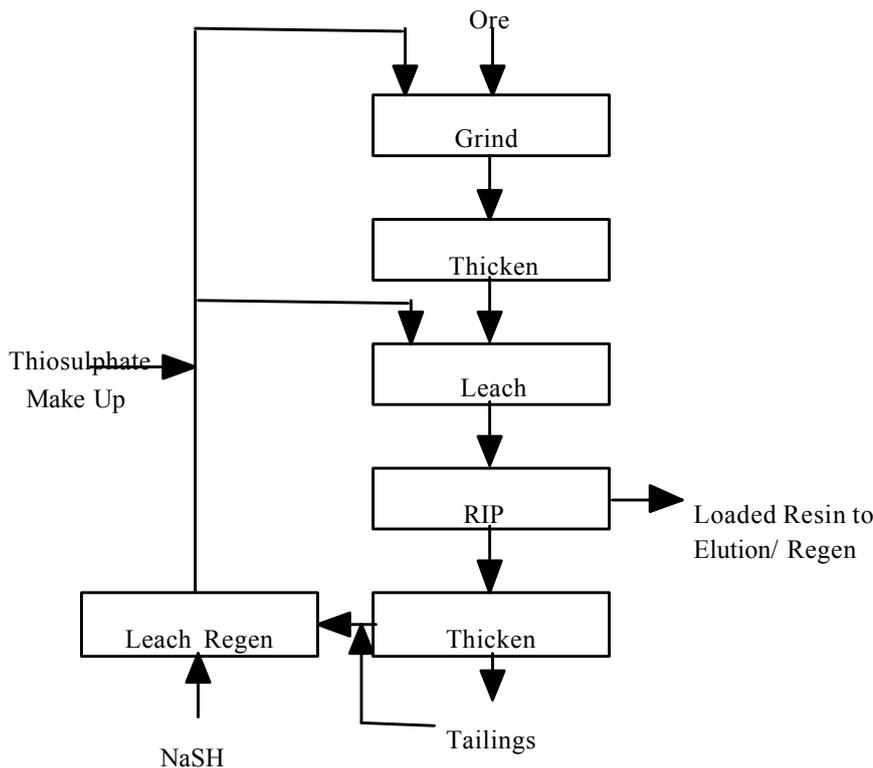


Figure 3. Overall Flowsheet

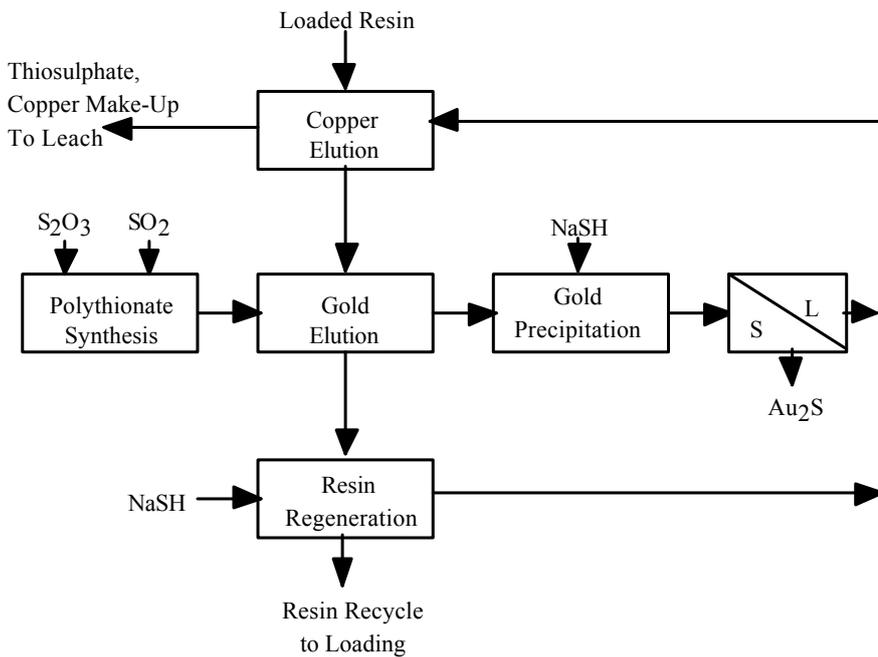


Figure 4. Resin Elution/Regeneration Flowsheet

### CONCLUSIONS

The double refractory ores of Barrick's Goldstrike operation have been found to be amenable to a process involving sulphide oxidation (by autoclaving), thiosulphate leaching and resin in pulp. The mild thiosulphate leaching conditions required for these ore types are compatible with efficient and economical gold recovery by adsorption on anion exchange resins. The economics of this process have been shown to be similar to the conventional cyanidation/CIL process that is used to treat the non preg-robbing ores at Goldstrike (unpublished SNC-Lavalin feasibility study).

These same conditions have been found to be suitable for ores from a few other mining companies as well, but are not universally applicable. In many cases, far more aggressive thiosulphate leaching conditions are needed to achieve gold recoveries that are comparable to the cyanidation process. These more aggressive leaching conditions are not compatible with resin in pulp because of competitive adsorption from the high concentrations of polythionates that are produced during leaching.

The gold elution process that was first developed for the Goldstrike flowsheet (involving thiocyanate displacement of gold thiosulphate by anion exchange) was fast and very efficient, even under ambient conditions. However, there were economic and environmental issues with this method of gold elution, and considerable effort has been invested in developing an alternative process.

A new gold elution/resin regeneration process has been developed, which involves the use of polythionate (tetra and trithionate anions) to displace the gold thiosulphate from the resin, by anion exchange. This process is also very efficient, achieving complete gold elution (>99%) in only a few hours, under ambient conditions. After elution, the resin is readily regenerated and restored to the activity and loading capacity of fresh resin. The entire resin cycle (loading, copper elution, gold elution, and regeneration) is carried out with

solutions that are in a near-neutral pH range, and resin losses due to osmotic shock are expected to be minimal.

All the compounds that are used in leaching and the new elution/regeneration processes are thiosalts, and no foreign ions are introduced at any stage. Chemistry has been developed and demonstrated at a bench scale for an overall scheme in which polythionates for gold elution are produced by oxidation of thiosulphate with sulphur dioxide, and the products from gold elution (eluate plus eluted resin) are then treated with sulphide ions to (a) recover the gold as a precipitate and (b) reduce the polythionates back to thiosulphate for leach liquor makeup. The consumables in this process are sulphur dioxide and sulphide ions.

This elution process and the associated sulphur chemistry have not yet been demonstrated in a continuous pilot plant over a number of loading/elution cycles.

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