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RECOVERY OF GOLD AND SILVER FROM OXIDATION LEACH RESIDUES BY AMMONIACAL THIOSULPHATE LEACHING

R.M.G.S. Berezowsky
Senior Research Metallurgist

and

V. B. Sefton
Manager

Chemical Metallurgy Research
Sherritt Research Centre
Sherritt Gordon Mines Limited
Fort Saskatchewan, Alberta, Canada

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RECOVERY OF GOLD AND SILVER FROM OXIDATION LEACH RESIDUES BY AMMONIACAL THIOSULPHATE LEACHING

R.M.G.S. Berezowsky and V.B. Sefton
Sherritt Gordon Mines Limited
Fort Saskatchewan, Alberta, Canada

An atmospheric ammoniacal thiosulphate leach system was developed to recover gold and silver from residues of the ammoniacal oxidation leaching of sulphidic copper concentrates. Extractions of 88 - 95% Au and 83 - 98% Ag were attained within 2 to 4 hours at 40 - 60°C in thiosulphate leaching of the oxidation leach residues of Manitoba chalcopyrite concentrates analyzing 24.6% Cu, 0.18 oz/ton Au and 4.26 oz/ton Ag and a complex British Columbia chalcopyrite/tetrahedrite concentrate analyzing 18.5% Cu, 0.27 oz/ton Au and 276 oz/ton Ag. Parameters affecting the Au and Ag solubilization included thiosulphate, ammonia, and cupric ion concentrations, temperature, retention time and the degree of Cu extraction and sulphide oxidation in the primary oxidation leach. The precious metals were recovered from the thiosulphate liquors by zinc dust cementation.

Introduction

In the ammonia/ammonium sulphate oxidation leaching of sulphide concentrates such as chalcopyrite for the recovery of copper at 50 to 120°C, some solubilization of gold and silver may occur during the early stages of the leach. As the degree of copper extraction and the oxidation of sulphide sulphur to sulphates and sulphamates approach completion, the precious metals report nearly quantitatively to the residues. Since Sherritt's Manitoba chalcopyrite concentrates contain appreciable amounts of gold and silver (0.11 - 0.23 oz/ton Au, 3.7 - 4.6 oz/ton Ag), an effective precious metals recovery scheme is a prerequisite for the ammonia oxidation leach to be competitive with pyrometallurgical or other hydrometallurgical processes.

A number of approaches have been examined for the treatment of the oxidation leach residues, including brine leaching, cyanidation and thiourea leaching. Most have been found inadequate due to low extractions, high consumption and cost of reagents, and incompatibility of the solvents with the main leach. One system which did meet all of the above requirements was the cupric-promoted ammoniacal thiosulphate leach.

Forward and Mackiw(1) had reported significant thiosulphate ion formation during the ammoniacal oxidation pressure leaching of copper-nickel-cobalt sulphide concentrates. The oxidation of sulphide sulphur was shown to proceed through a series of reactions involving the formation of thiosulphate, with subsequent oxidation to thionates which in turn were oxidized to sulphate and sulphamate. They had also found soluble copper to be an effective catalyst for the sulphur oxidation reactions. Other workers had noted the dissolution of small quantities of gold and silver during the early stages of the oxidation leaching of a number of sulphides and had attributed this to the initial presence of thiosulphate ions(2,3). Kakovskii(4) presented a thermodynamic analysis of the dissolution of noble metals in ammoniacal and thiosulphate systems. Subsequent experimental investigations by Tyurin and Kakovskii(3) with thiosulphate, ammoniacal and mixed ammoniacal thiosulphate systems tended to support the mechanisms whereby gold was solubilized solely as a thiosulphate complex

$$4Au^\circ + 8S_2O_3^{2-} + 2H_2O + O_2 \rightleftarrows 4Au(S_2O_3)_2^{3-} + 4OH^- \qquad (1)$$

while silver was solubilized predominantly as the thiosulphate complex

$$4Ag^\circ + 8S_2O_3^{2-} + 2H_2O + O_2 \rightleftarrows 4Ag(S_2O_3)_2^{3-} + 4OH^- \qquad (2)$$

with a relatively small portion forming the ammine complex

$$4Ag^\circ + 8NH_3 + 2H_2O + O_2 \rightleftarrows 4Ag(NH_3)_2^{+} + 4OH^- \qquad (3)$$

Copper ions were reported to exhibit a strong catalytic effect on the rates of dissolution of the noble metals. In a more recent study of the dissolution of elemental gold in ammoniacal sodium thiosulphate solution, Umetsu and Tozawa(5) confirmed and extended the previous investigations, covering a temperature range of 18 to 180°C.

While the preceding studies reported significant data on the thiosulphate leaching of noble metals, these were conducted in relatively pure systems with elemental gold and silver and primarily under pressure. The present paper describes laboratory work leading to the adaptation of an atmospheric thiosulphate leach system for the extraction of the trace quantities of gold and silver present in leach residues comprising predominantly hydrated ferric oxides and unleached sulphides. The extraction of gold directly from the copper concentrate was also found feasible and is also briefly described. Several recovery routes for the dissolved precious metals were investigated and an overall flowsheet for the extraction and recovery of the precious metals, integrated with the main oxidation pressure leach for copper, is proposed.

Experimental

Materials

Primary Ammoniacal Oxidation Pressure Leaching. Most of the testwork was conducted with copper concentrates from Sherritt's Ruttan and Fox Mines in Northern Manitoba, either individually or as a 3:1 blend. The concentrate compositions are given in Table I. Mineralogically, they comprised chalcopyrite, pyrite, sphalerite and pyrrhotite. Most of the leaching was with the concentrates as received, with 60% minus 44 μm. A number of tests were also conducted with a complex tetrahedrite/chalcopyrite concentrate of high silver content from British Columbia whose composition is also given in Table I.

Oxidation Leach Residues for Precious Metals Recovery. The residues from the oxidation of the Manitoba concentrates corresponded to primary leach dissolutions of 93 to 98.5% Cu and comprised predominantly hydrated iron oxides, pyrite, "unsolubilized" Cu and Zn and virtually all of the initial gold and silver. Depending on the primary leach conditions, at 97 - 98.5% Cu dissolution (and approximately 60% Zn), some 60 to 95% of the residual Cu (and approximately one-third of the Zn) was actually in the oxidic form, either coprecipitated with or adsorbed on the hydrated ferric oxide. Identification of the gold and silver species was not attempted. The residue compositions are presented in Table I.

Table I. Analysis of Concentrates and Leach Residues Employed in Present Study

	Copper Concentrates			Ammoniacal Oxidation Leach Residues			
	Feed to Oxidation Pressure Leaching			Feed to Precious Metals Recovery Leach			
	Ruttan/Fox		B.C.	Ruttan/Fox		B.C.	
Element	Range	Average		Range	Average	Range	Average
Cu (%)	23.2 - 25.3	24.6	18.5	0.54 - 2.58	1.36	0.47 - 2.22	1.32
Zn (%)	1.80 - 4.45	3.56	1.86	1.14 - 4.27	2.30		
Fe (%)	29.7 - 32.3	30.3	24.4	46.5 - 54.1	50.5	31.9 - 36.1	35.0
S_T (%)	32.8 - 36.4	34.3	38.8	7.87 - 18.0	14.2	20.2 - 30.7	25.7
Au (oz/ton)	0.113 - 0.234	0.177	0.27	0.15 - 0.40	0.289	0.34 - 0.40	0.38
Ag (oz/ton)	3.70 - 4.60	4.26	276	5.15 - 8.39	6.82	349 - 404	373
% minus 44 μm	57 - 63	60	50		70		
% minus 20 μm	16 - 25	20	18		60		
% minus 5 μm	5 - 10	8	3		50		

Equipment and Procedures

Ammoniacal Oxidation Pressure Leaching. The majority of the leaches were conducted in titanium, stainless steel, or lead-lined autoclaves of 2.5 ℓ operating capacity. The temperature was controlled externally by a gas burner or water spray. Measured quantities of concentrate (usually 250 g/ℓ), ammonium sulphate, water and ammonium hydroxide (to 130 g/ℓ NH_3) were charged to the autoclave, heated to a predetermined temperature and the desired oxygen overpressure was applied and maintained. Operating temperatures ranged from 49 to 104°C while the oxygen overpressure was generally 20 psi.

Thiosulphate Leaching. Generally, 400 g of residue (or concentrate) were repulped with 1 ℓ of ammonium thiosulphate solution and leached in a 2 ℓ pyrex beaker equipped with baffles, heating tape, thermometer, gas sparge tube and overhead agitator. Cupric ion, when added, was supplied as primary leach liquor, or on occasion was already present with unwashed oxidation leach residue.

Cyanidation. Washed residues were leached at 200 g/ℓ at 23°C in an open bottle on rollers for a total of 48 hr, with pH and free cyanide adjustment to 10.5 and 1 g/ℓ respectively every 4 hr.

Brine Leaching. Washed residues were leached at 500 g/ℓ solids at 100 - 105°C in 250 g/ℓ NaCl with pH adjustment to 1.5 - 2.5 with HCl.

Thiourea Leaching. Washed residues were leached at 250 g/ℓ solids at 23°C in 25 g/ℓ thiourea with pH adjustment to 3-4 with H_2SO_4 and the addition of H_2O_2, at approximately 2 g/kg of residue.

Recovery of Precious Metals From Thiosulphate Leach Liquors. Numerous recovery routes were examined including direct sulphide precipitation or elevated temperature, elevated pressure, high-pH oxidation of the liquor followed by Au and Ag recovery by cementation, carbon adsorption, and/or sulphide precipitation, with or without prior removal of Cu by Solvent Extraction or Ion Exchange. The preferred route, however, involved direct cementation with zinc dust under atmospheric conditions; prior reduction of any remaining Cu^{2+} to Cu^{+} was conveniently accomplished with SO_2.

Results and Discussion

Dissolution of Precious Metals During the Ammoniacal Oxidation Pressure Leaching of Ruttan/Fox Chalcopyrite

The results of a rate of study of the ammoniacal oxidation pressure leaching of chalcopyrite concentrate at 65°C are illustrated in Figure 1 and show appreciable dissolution of gold - up to 27% at a corresponding copper extraction of 45%. Thereafter, the extraction of gold declined, and had this leach been extended beyond 90% Cu extraction, a near-negligible extraction of gold would have been observed. Paralleling the behaviour of gold was the level of unsaturated sulphur species (predominantly thiosulphate and various thionates) denoted here by the Bromate Value* which reached a peak value of 1630 and generally decreased to <10 by the end of such leaches. Silver solubilization had not been observed.

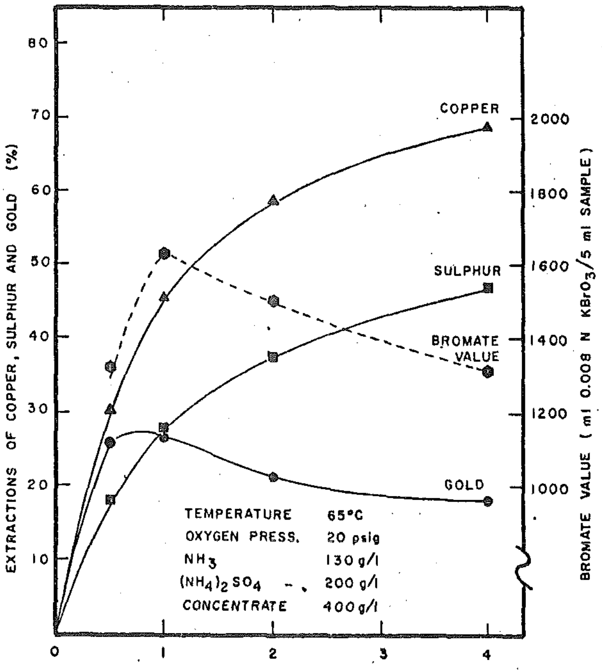

Figure 1. Solubilization of Gold During Ammonia/Ammonium Sulphate Oxidation Pressure Leaching of a Ruttan/Fox Chalcopyrite Blend

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* mls of 0.008 N $KBrO_3$ required to titrate a 5 ml sample of leach liquor.

These results indicated that whereas in single stage or multi-stage cocurrent leaches the precious metals will report predominantly to the residues, in a multi-stage countercurrent leach, the product liquor may contain appreciable levels of Au. The oxidation leaches in this study were, however, single-stage batch leaches.

Distribution of Gold and Silver in Oxidation Leach Residue Fractions

The results of the separations of the oxidation leach residues into sulphidic and oxidic fractions by flotation, elutriation and screening are summarized in Table II and indicate little or no upgrading of the gold and silver in either fraction. The recovery of the precious metals therefore required hydrometallurgical treatment of the entire residue.

Table II. Distribution of Silver and Gold in Leach Residue Fractions; Ammoniacal Oxidation Pressure Leaching of Ruttan/Fox Chalcopyrite Concentrate

		Assays					Distributions of Residue Fractions					
		(% or oz/t)					(%)					
Separation	Product	Cu	Fe	S	Ag	Au	Wt.	Cu	Fe	S	Ag	Au
Flotation	Copper Concentrate	24.9	32.3	36.4	4.60	0.234						
	Leach Residue$^{1)}$	1.96	51.4	15.4	7.18	0.385	100	100	100	100	100	100
	Residue Float Conc.	2.78	44.7	33.1	8.08	0.498	33.0	47.9	28.4	79.3	39.0	43.5
	Residue Float Tails	1.50	55.7	4.26	6.25	0.320	67.0	52.1	71.6	20.7	61.0	56.5
Elutriation	Copper Concentrate	24.5	29.9	34.8	4.25	0.166						
	Leach Residue$^{2)}$	2.52	48.1	16.3	6.42	0.257	100	100	100	100	100	100
	U/F Solids (Sulphides)	7.08	36.6	39.1	8.28	0.157	25.6	71.9	19.4	61.7	32.3	16.3
	O/F Solids (Oxides)	0.95	52.2	8.32	5.95	0.278	74.4	28.1	80.6	38.3	67.7	83.7
Screening	Copper Concentrate	24.2	30.0	34.3	4.25	0.173						
	Leach Residue$^{3)}$	4.64	45.5	18.3	6.71	0.254	100	100	100	100	100	100
	Plus 44 μm	9.79	35.5	39.8	4.58	0.155	27.8	59.2	21.5	59.8	18.8	17.3
	Minus 44 μm	2.60	50.0	10.3	7.61	0.285	72.2	40.8	78.5	40.2	81.2	82.7

Primary Ammonia Oxidation Leach Conditions and Extractions

1) 104°C, 3 h, 20 psig O_2; extractions (%) 95.1 Cu, 56.7 Zn, 73.4 S_T, negligible Ag and Au
2) 98°C, 6 h, 20 psig O_2; extractions (%) 93.6 Cu, 47.3 Zn, 70.9 S_T, negligible Ag and Au
3) 82°C, 6 h, 20 psig O_2; extractions (%) 87.4 Cu, 42.6 Zn, 64.8 S_T, negligible Ag and Au

Brine, Cyanide and Thiourea Leaching of Ruttan/Fox Residues

Brine leaching extracted up to 99% of the residual silver; there was an indication of a dependence of the silver recoverability on the degree of prior copper extraction and sulphide oxidation (Table III). Gold extractions, however, were very low attaining at most only 15% with a chlorine sparge. This was attributed to the relatively high sulphide content of the residues.

Cyanidation of the total residue solubilized 68.8 and 87.7% of the gold after 25 and 48 hours but only 30.9 and 50.4% of the silver, respectively (Table III). Cyanide and lime consumptions were high at 64 and 54 lb/ton due, at least in part, to the co-extraction of appreciable residual copper. It

Table III. Extraction of Gold and/or Silver From Ammoniacal Oxidation Leach Residues by Various Secondary Leach Systems

BRINE LEACHING

Conditions: 500g residue/ℓ, 250 g/ℓ NaCl, pH 2.0 - 2.5, 102°C, 2 h.

Ammonia Oxidation Leach		Brine Leach
Temperature (°C)	Cu Extraction (%)	Ag Extraction (%)
52	78.6	82.6
	92.7	91.1
105	97.4	98.6
138	98.1	99.0

CYANIDATION

Conditions: 23°C, pH 10.5, ~1 g/ℓ free cyanide.

Cyanide Leach Feed		Time	Extractions (%)			Consumption (lbs/t)	
Solids	(g/ℓ)	(h)	Cu	Ag	Au	NaCN	CaO
Total Residue 1)	200	25 48	53.1 62.7	30.9 50.4	68.8 87.7	53 64	44 54
Oxide-Free Residue 2)	75	25 48	42.4 66.2	80.2 92.1	83.2 87.5	83 96	34 34

1) Ammonia oxidation leach extractions (%) 95.0 Cu, 56.7 Zn, 73.4 S_T
• residue assays (%) 1.96 Cu, 1.24 Zn, 51.4 Fe, 15.4 S_T,
(oz/t) 7.18 Ag, 0.385 Au.

2) Previous residue after dissolution of oxidic fraction in H_2SO_4/SO_2; wt. loss ~65%
• residue assays (%) 2.29 Cu, 2.89 Zn, 35.5 Fe, 47.4 S_T,
(oz/t) 21.4 Ag, 1.17 Au.

THIOUREA LEACHING

Conditions: 250 g solids/ℓ, 25 g/ℓ thiourea, 25°C, pH 3-4 (H_2SO_4), oxidant (H_2O_2)

Time	Extractions (%)					
	Residue A 1)		Residue B 2)		Unleached 3) Concentrate	
(h)	Au	Ag	Au	Ag	Au	Ag
1			86.3	67.2	69.8	~0
2	78.4	66.0	88.0	61.1	78.2	~0
4	83.4	55.9	91.5	56.6	83.1	~0
6	85.5	50.4				

1) NH_3/O_2 Leach Extractions (%) 95.0 Cu, 73.4 S_T;
Residue Assays (%) 1.96 Cu, (oz/t) 7.18 Ag, 0.385 Au.

2) NH_3/O_2 Leach Extractions (%) 95.7 Cu, 77.4 S_T;
Residue Assays (%) 1.77 Cu, (oz/t) 8.39 Ag, 0.40 Au

3) Concentrate Assays (%) 24.9 Cu, 32.3 Fe, 1.8 Zn, 36.4 S, (oz/t) 4.60 Ag, 0.234 Au.

appears that a significant portion of the residual silver had been associated with the precipitated ferric oxides, as a SO_2/H_2SO_4 treatment of the residue to dissolve the oxides prior to cyanidation markedly improved the silver extractions to 80.2 and 92.1%, respectively. The leach rate of gold was also improved but the eventual extraction after 48 hours remained the same at 87-88%.

Thiourea leaching has been described in a number of publications(6,7). Leaching of the present residues in an acidified thiourea solution with moderate amounts of hydrogen peroxide attained extractions of 91.5% of the gold and 67.2% of the silver (Table III). However, some of the solubilized silver subsequently precipitated before the maximum gold extraction had been attained. Direct thiourea leaching of the chalcopyrite concentrate was also attempted and extracted 83.1% of the gold but negligible amounts of silver.

While the preceding approaches proved interesting and showed some promise, they were abandoned for reasons of unacceptable overall recoveries of gold and silver, high reagent consumptions and costs, an incompatibility of the solvent with the ammonia/ammonium sulphate system of the main leach and primarily because of the more favorable results obtained with the ammoniacal thiosulphate system.

Thiosulphate Leaching of Ruttan/Fox Oxidation Leach Residues

Effects of Primary Oxidation Leach Extractions and of Presence of Soluble Cupric Ion. The rate curves for the thiosulphate leaching of two residues corresponding to oxidation leach extractions of 93.3 and 98.6% Cu are presented in Figure 2; the assays of the washed oxidation residues were

No. 1: (%) 2.58 Cu, 4.27 Zn, 46.7 Fe, 16.7 S_T, (oz/t) 0.284 Au, 6.71 Ag
No. 2: (%) 0.59 Cu, 3.03 Zn, 49.2 Fe, 17.5 S_T, (oz/t) 0.301 Au, 7.06 Ag

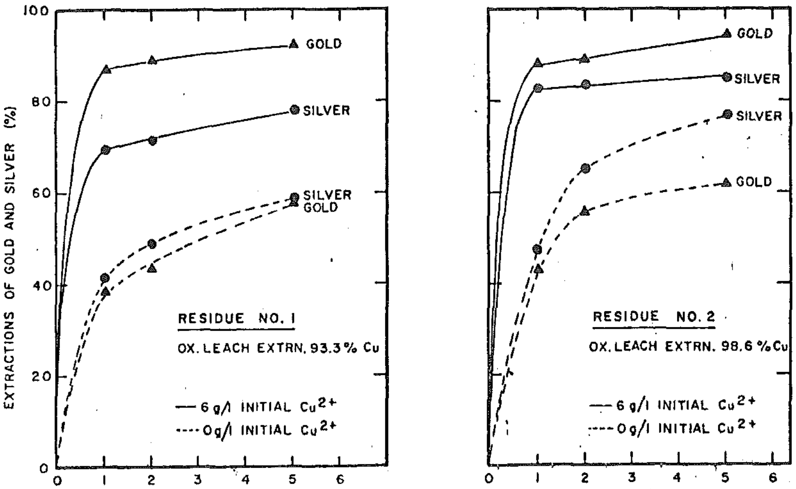

Figure 2. Thiosulphate Leaching of Gold and Silver From Ammoniacal Oxidation Leach Residues

Conditions: Nitrogen purge, pH 8.5 - 9.7, 49°C, 100 g/ℓ $(NH_4)_2S_2O_3$, 135 g/ℓ residue

In each case, one portion of the oxidation leach residue slurry had been thoroughly washed while a second portion had been thickened to 50% solids without washing, to provide an initial level of 6 g/ℓ Cu^{2+} when repulped in the thiosulphate leach liquor. The thiosulphate leach results show that:

- the presence of the Cu^{2+} markedly improved the solubilization of both gold and silver, particularly the gold

- in the presence of Cu^{2+}, gold extractions from the two residues were identical, indicating no dependence on the prior oxidation leach

- the extraction of silver depended on the prior degree of copper extraction and sulphide oxidation in the primary leach.

The maximum extractions of 94.0% Au and 84.7% Ag were therefore obtained in the presence of Cu^{2+} from the second residue.

Effects of Pulp Density and Initial Cupric Ion Levels. Thiosulphate leach rate curves for a residue representing a 98.6% Cu extraction and assaying (%) 0.54 Cu, 1.87 Zn, 50.4 Fe, 7.87 S_T and (oz/t) 0.15 Au and 5.15 Ag are presented in Figures 3, 4 and 5; the oxidation residue had been thickened and filtered to 80% solids but had not been washed. The results of a pulp density series at 200, 400 and 600 g/ℓ solids, with corresponding initial Cu^{2+} levels of 2.25, 4.50 and 6.75 g/ℓ respectively in the thiosulphate leach slurry, are summarized in Figure 3.

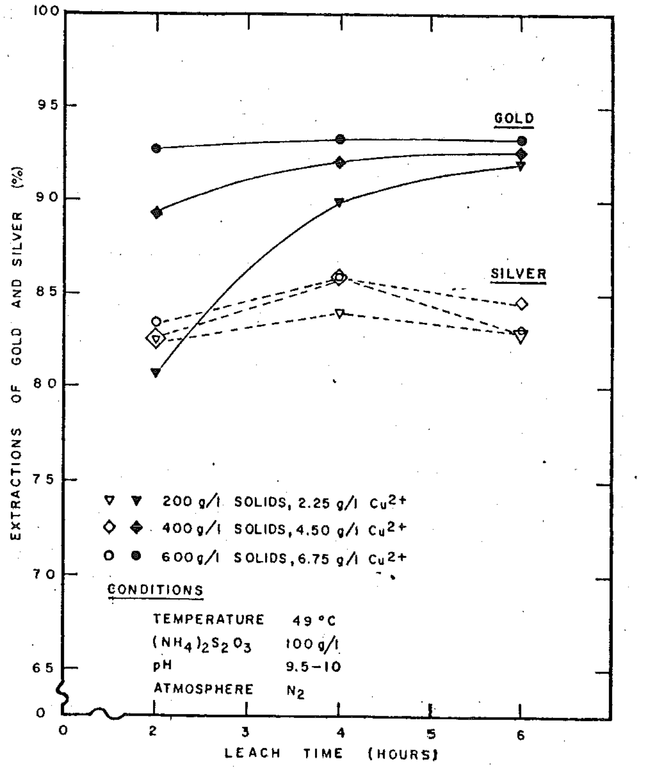

Figure 3. Effect of Pulp Density and Initial Cu^{2+} on the Thiosulphate Extractions of Gold and Silver From Ammoniacal Oxidation Leach Residue

There was an improvement in the leaching of gold with increasing solids contents but this was attributed primarily to the increasing Cu^{2+} levels rather than the solids content. Silver extractions were not significantly affected. The final (6 hr) extractions of gold and silver ranged from 92 to 93.3% and 82.9 to 84.7% respectively.

Effect of Temperature (Figure 4). Increasing the temperature from 38 to 60°C apparently improved gold extractions, but only marginally. The rates of silver extraction were improved initially, but the higher temperatures also promoted the eventual precipitation of the solubilized silver.

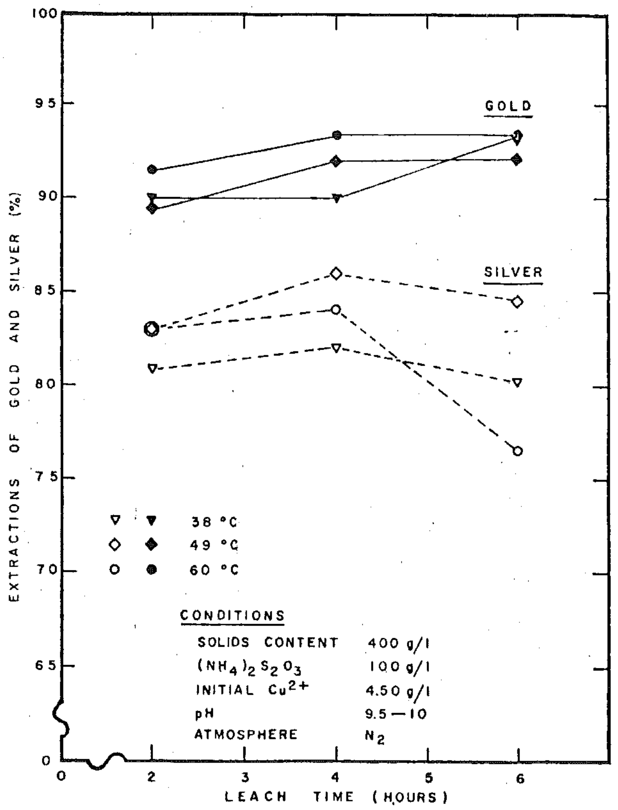

Figure 4. Effect of Thiosulphate Leach Temperature on the Extractions of Gold and Silver From Ammoniacal Oxidation Leach Residue

Effect of Ammonium Thiosulphate Concentration (Figure 5). Increasing the thiosulphate levels from 50 to 200 g/ℓ depressed the gold solubilization slightly (from 96.0 to 92.7% after 6 hr) but at the same time improved silver solubilizations marginally from 83.5 to 88.7% after 4 hr and 83.5 to 85.8% after 6 hr.

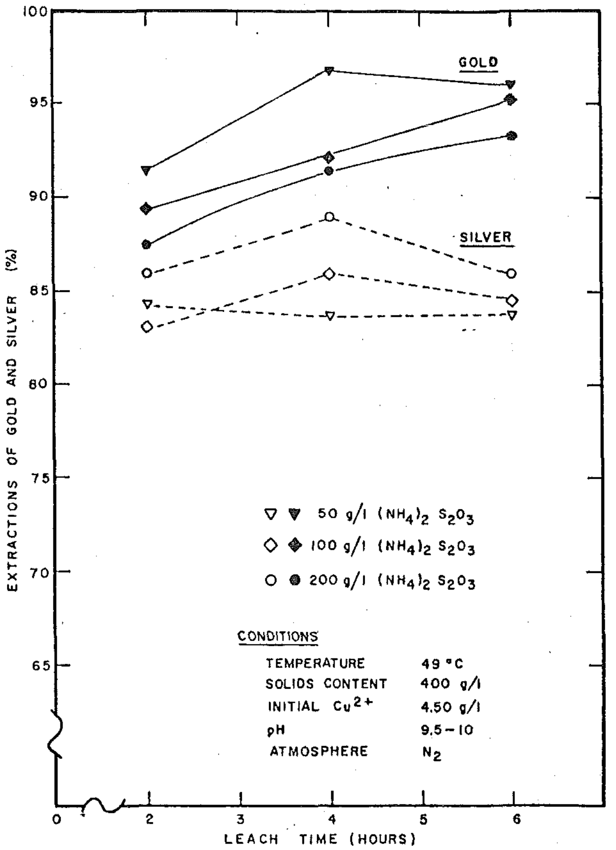

Figure 5. Effect of Ammonium Thiosulphate Concentration on the Extractions of Gold and Silver From Ammonia Oxidation Leach Residues

Effect of Ammonia. Sufficient free NH$_3$ is required to meet the requirements of Cu(NH$_3$)$_4$$^{2+}$; operating with a slight excess of NH$_3$, at pH 10.0 - 10.5 proved marginally better, particularly in the case of silver, than at pH 9.0 - 9.5.

Based on the available testwork, conditions recommended for the thiosulphate leaching to extract 92-94% Au and 83-86% Ag from the present Ruttan/Fox concentrates may be summarized as follows; 98% or better copper extraction in the primary ammoniacal oxidation pressure leach, thiosulphate leaching at 400 - 600 g/ℓ solids, 3 - 5 g/ℓ initial Cu^{2+}, 50 - 100 g/ℓ $(NH_4)_2S_2O_3$, pH $\sim$10, 3-5 hr at 35-50°C.

Thiosulphate Leaching of British Columbia Leach Residue

The residues prepared in a similar manner from the British Columbia concentrate were also amenable to thiosulphate leaching, as shown by the results in Table IV.

Table IV. Thiosulphate Leaching of Residues From B.C. Concentrate

Test No.	Material	Assays (%)	Assays (oz/t)		Extractions (%)	
		Cu	Au	Ag	Au	Ag
1	Thiosulphate Leach Feed	1.50	0.34	365		
	Thiosulphate Leach Residue		0.04	9.8	88.8	98.3
2	Thiosulphate Leach Feed	0.47	0.38	349		
	Thiosulphate Leach Residue		0.026	28.2	93.2	93.0

Direct Ammoniacal Thiosulphate Leaching of Ruttan/Fox Concentrates

In view of the successful results with leach residues, direct thiosulphate leaching of the chalcopyrite concentrate was also investigated, since handling of these solids would be much preferred to that of the ferric oxide-containing leach residues. In the presence of an initial 3-5 g/ℓ Cu^{2+} and with mild air sparging gold extractions as high as 97% were attained. Silver extractions, at best, were only 33%. To achieve a high recovery of both gold and silver from these concentrates therefore apparently required prior oxidation leaching. A brief discussion of the results obtained on the direct thiosulphate leaching of the concentrates is nevertheless presented, in the event that there may exist concentrates whose relative gold and silver values would justify direct processing to primarily recover the gold.

Effect of Initial Cupric Concentration and Leach Atmosphere. Gold extractions were very dependent on initial Cu^{2+} levels, particularly in a nitrogen atmosphere as illustrated in Figure 6 and required 3-5 g/ℓ for approximately 90% Au extraction.

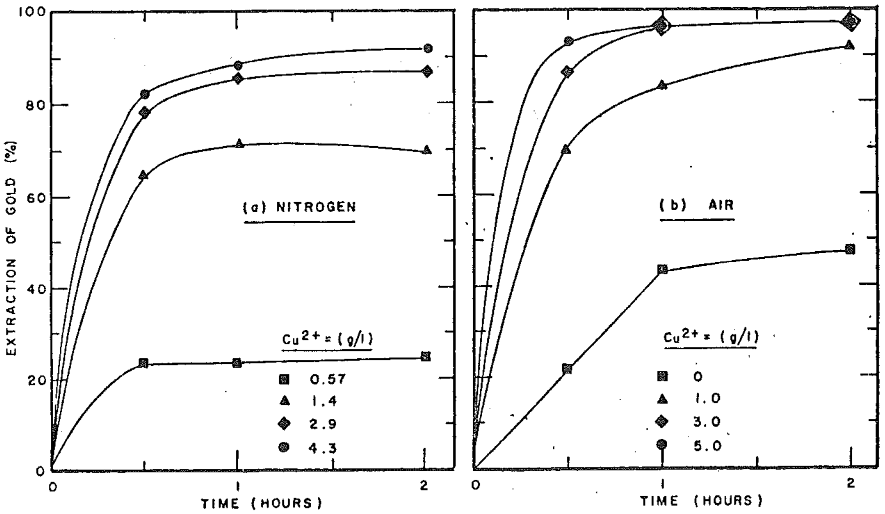

Figure 6. Effects of Initial Cupric Concentration and Leach Atmosphere on the Extraction of Gold From Ruttan/Fox Chalcopyrite Concentrate

a) Nitrogen purge, 49°C, pH 9 - 10, 130 g/ℓ $(NH_4)_2S_2O_3$, 400 g/ℓ concentrate: 25.3% Cu, 0.188 oz/ton Au.
b) Air sparge, 50°C, pH 9.9 - 10.1, 100 g/ℓ $(NH_4)_2S_2O_3$, 400 g/ℓ concentrate: 24.3% Cu, 0.168 oz/ton Au.

A mild air sparge was preferred in that it enabled higher gold extractions at lower initial Cu^{2+} levels by virtue of maintaining at least a portion of soluble copper as cupric and by promoting the in situ generation of additional soluble Cu from the concentrate as shown below in Table V:

Table V. Effects of Initial Cupric Concentration and Leach Atmosphere on the Leaching of Gold From Chalcopyrite Concentrate

Nitrogen Atmosphere				Air Sparge			
Soluble Copper (g/ℓ)			Gold Extraction	Soluble Copper (g/ℓ)			Gold Extraction
Initial	Final	Change	(%)	Initial	Final	Change	(%)
0.57	0.39	-0.18	11.7	0	0.68	+0.68	55.4
1.44	2.21	+0.77	68.6	0.98	2.05	+1.07	92.3
2.87	3.52	+0.65	86.2	2.95	4.15	+1.20	96.8
4.30	5.13	+0.83	91.5	4.97	6.37	+1.40	97.0

Effect of Temperature and Leach Atmosphere. Increasing the leach temperature from 25 to 82°C improved the initial gold extraction rates. However, temperatures in excess of 60°C promoted subsequent precipitation of copper (as either cuprous or cupric sulphide) and with it appreciable quantities of the solubilized gold (Figure 7 and Table VI).

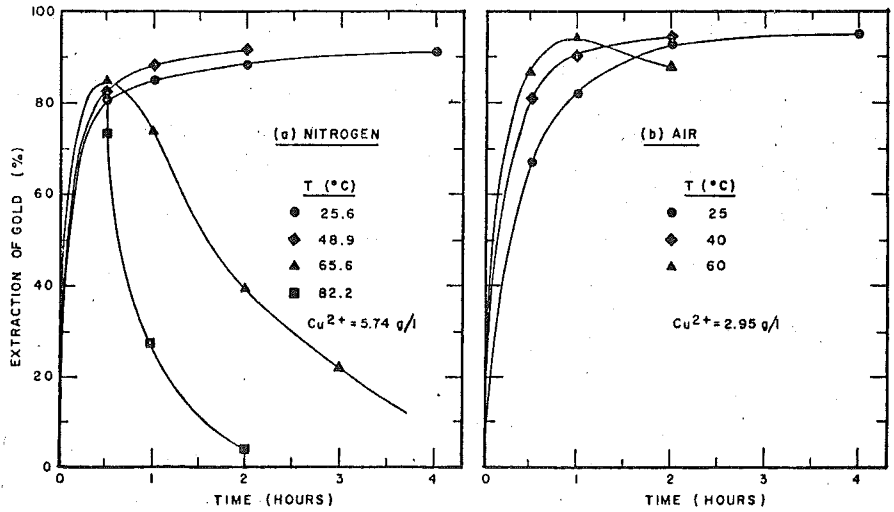

Figure 7. Effects of Temperature and Leach Atmosphere on the Extraction of Gold From Ruttan/Fox Chalcopyrite Concentrate

a) Nitrogen purge, pH 9.2 - 10.2, 130 g/ℓ $(NH_4)_2S_2O_3$, 400 g/ℓ concentrate: 25.3% Cu, 0.188 oz/ton Au.
b) Air sparge, pH 10 - 10.2, 50 g/ℓ $(NH_4)_2S_2O_3$, 400 g/ℓ concentrate: 24.3% Cu, 0.168 oz/ton Au.

The presence of an air sparge slightly offset this tendency of copper precipitation but a temperature range of 25 - 50°C appears preferable for the direct leaching.

Table VI. Effects of Leach Temperature and Atmosphere on the Leaching of Gold From Chalcopyrite Concentrate

Nitrogen Atmosphere					Air Sparge				
Temp.	Soluble Copper (g/ℓ)			Gold Extrn.	Temp.	Soluble Copper (g/ℓ)			Gold Extn.
(°C)	Initial	Final	Change	(%)	(°C)	Initial	Final	Change	(%)
25.6	5.74	6.70	+0.96	90.4	25	2.95	6.30	+3.35	95.2
48.9	4.30	5.13	+0.83	91.5	40	2.95	5.28	+2.33	94.6
65.6	5.74	0.38	-5.36	22.3	60	2.95	3.30	+0.35	88.1
82.2	5.74	0.28	-5.46	8.0					

Thiosulphate and ammonia concentrations and the concentrate particle size were also found to affect the solubilization of gold; some of these results have been reported elsewhere(8). It is noteworthy, however, that grinding of the concentrates for 0.25 to 2 hr in a ball mill prior to direct thiosulphate leaching had an effect similar to that of the increased temperature; the initial leach rates of gold were increased, but the freshly-generated, reactive sulphide surfaces apparently promoted reduction and precipitation of the copper and with it, some of the solubilized gold.

Stability of Thiosulphate During Residue and Concentrate Leaching

The thiosulphate ions can undergo a variety of complex degradative reactions, particularly in the presence of sulphides and soluble copper. In this study, the leach conditions were purposely mild, with initial testwork under nitrogen to minimize the oxidation of the thiosulphate. Although identification of any of the possible degradation products was not attempted, analysis of the liquors for $S_2O_3^{=}$ indicated that under the recommended conditions some 90 - 95% of the thiosulphate was accounted for and could be recycled.

Precious Metals Recovery From Leach Liquors

Cementation with zinc dust was selected as the route for the recovery of the gold and silver from the thiosulphate leach solutions. Since a major portion of the zinc would be consumed by cupric ion, it is advisable that as much as possible of the soluble copper in the product liquor be in its reduced state prior to the cementation. This may be readily accomplished by staging of the thiosulphate leach and allowing for the reduction of cupric copper by the sulphides or thiosulphate. Any remaining cupric ion in the liquor after separation from the leach residue was conveniently reduced by sulphur dioxide.

Some of the testwork with zinc dust cementation is summarized in Table VII. In the laboratory tests, the soluble copper content of most of the leach product slurries was predominantly cuprous, but the Cu^+ was reoxidized rapidly upon exposure of the filtered solutions to the atmosphere. As a result, the feed solution to these cementations contained copper primarily in the cupric state.

Table VII. Recovery of Gold and Silver by Zinc Dust Cementation

Solution Pretreatment	Zinc Dust (g/ℓ)	Cement Product (g/ℓ)	Filtrate Assays				Recovery (%)	
			pH	Cu_T (g/ℓ)	Au (mg/ℓ)	Ag (mg/ℓ)	Au	Ag
Pregnant liquor			10.2	6.76	2.20	36.8		
– none	10	14.4	9.75	0.004	<0.05	2.1	>98	94.2
	6	7.6	9.9	0.125	<0.05	1.9	>98	94.8
	2	0.40	10.0	6.57	1.94	19.6	11.8	46.7
SO_2 to pH 8	6	8.3	8.25	0.048	<0.05	1.9	>98	94.8
	2	3.48	8.70	3.44	<0.05	1.9	>98	94.8

Although it is evident that some selectivity in the cementation of the precious metals can be achieved relative to the copper, the product will nevertheless contain appreciable copper and zinc. As such, it should be a suitable reductant for the cupric ion prior to the zinc dust cementation, while at the same time the precious metals content of the product would be upgraded. Further upgrading of either the original or recycled cement product may also be accomplished by selective dissolution of the copper and zinc in a separate small oxidizing leach.

Flowsheet

On the basis of the laboratory work on the thiosulphate leach, a generalized flow diagram incorporating the primary oxidation leach, the secondary leach of the residue with thiosulphate and the recovery of the precious metals from solution is shown in Figure 8.

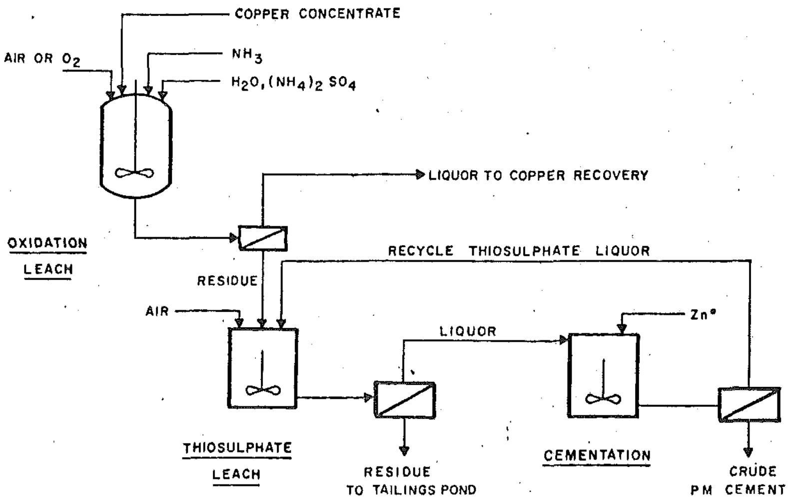

Figure 8. Flow Diagram For Recovery of Copper, Gold and Silver From Chalcopyrite Concentrate

Typically, chalcopyrite concentrate is leached in an ammonia/ammonium sulphate solution at 80-120°C under 20-50 psi oxygen overpressure for 2-5 hr to 98% or higher copper extraction. The product slurry undergoes a liquid/solids separation incorporating thickening and/or filtration, with the pregnant liquor proceeding to copper recovery by hydrogen reduction, solvent extraction/electrowinning or other means. The partially washed, filtered residue is further processed in a leach with ammoniacal thiosulphate solution under atmospheric conditions at 25-50°C for 2-5 hr; a level of 3-5 g/ℓ soluble copper to promote the leach is provided with recycle thiosulphate liquor and/or as entrained primary oxidation leach liquor with the primary leach solids. Air may be provided during the initial stages of the thiosulphate leach to ensure a working level of Cu^{2+}, but the reaction is staged such that the major portion of the soluble copper in the product liquor is in the reduced cuprous state. After a liquid/solids separation, any remaining cupric copper is preferably reduced with SO_2 or recycled cement product, and the precious metals are recovered from the thiosulphate liquor with zinc dust cementation at 25°C.

The precious metals product may be upgraded in a separate small leach under mildly oxidizing conditions for selective dissolution of contained copper and zinc. The bulk of the thiosulphate liquor depleted of precious metals is suitable for recycling; control of the build-up of copper and zinc and the ammonium sulphate entering from the oxidation leach with the primary leach solids is by H_2S precipitation and/or by bleeding to the primary leach circuit.

Conclusions

Extraction of gold and silver from the residues of a primary ammoniacal oxidation leach of chalcopyrite concentrates was effectively accomplished by a secondary leach in ammoniacal thiosulphate solution. The thiosulphate leach system not only attained higher extractions than conventional methods such as cyanidation or brine leaching, but is environmentally preferable since bleed streams are readily accommodated in the primary oxidation leach system.

Parameters have been defined for the thiosulphate extraction of 92 - 94% Au and 83 - 87% Ag from residues previously oxidation-leached to 96 - 98% Cu extraction from Sherritt's Manitoba chalcopyrite concentrates containing 24.6% Cu and 0.18 oz/ton Au and 4.26 oz/ton Ag. Direct thiosulphate leaching of the concentrates was also shown capable of extracting up to 97% of the gold but only 33% of the silver. Since the objective was a high overall precious metals recovery, thiosulphate leaching of the oxidation leach residues was the preferred route. The amenability of oxidation leach residues of other copper concentrates to the thiosulphate leach was also demonstrated.

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