ORE DRESSING INVESTIGATIONS

TR17-164-172

R.593. Separation tests, copper-tin flotation concentrate, Luina.

Cleveland Tin N.L., Luina, submitted samples of copper-tin flotation concentrate, Reg. Nos. 691183 and 713144. The samples were assayed and gave the following results:

	Assay (%)			*Assay (%)*	
Element	*691183*	*713144*	*Element*	*691183*	*713144*
Cu	21.8	18.0	As	0.1	
S.Sn	3.8	2.84	Sb	0.1	
C.Sn	0.33	0.42	Bi	0.24	
S	34.4	36.4	Insoluble	1.33	
Fe	35.4		Ag	0.017	
Zn	0.58		Total	98.3	

Note: Ag 0.017% = 170 g/t

From the assay the approximate sulphide mineral composition was calculated to be chalcopyrite 60%, pyrite 20% and stannite 6%.

From the analysis and current metal prices the copper content is valued at about twice that of the tin, that is 70% of the value is due to copper and 30% of the value is due to tin.

TREATMENT METHOD

Because the major source of value stems from the copper content of the sample an endeavour to separate and recover all the copper was the prime objective.

Some possible methods of chemical treatment are outlined in Table 1. The leaching method was selected, as this was the least costly. Two types of test were carried out:

(1) Direct leaching.
(2) Leaching of the roasted concentrate.

The general effect of time, temperature and particle size on the leach using various solutions are given by Haver and Wong (1971). The leach operating conditions in these tests are outlined in Table 2.

The leach operations were conducted as outlined below:

Test	*Material*	*Size*	*Solvent*
A.1	RD	89% -52 µm[1]	10% H_2SO_4
A.2	RD	89% -52 µm	Titan effluent†
B.1	FC	85% -52 µm[2]	Titan effluent†
B.2	FC	85% -52 µm	$FeCl_3.6H_2O$ with Titan effluent
B.3*a*	FC	85% -52 µm	$FeCl_3.6H_2O$ with 10% HCl (v/v)
B.3*b*	FC	85% -52 µm	$FeCl_3.6H_2O$ with 20% HCl (v/v)
B.4*a*	FC	85% -52 µm	$FeCl_3.6H_2O$ with 2% HCl (v/v)
B.4*b*	FC*	88% -52 µm	$FeCl_3.6H_2O$ with 5% HCl (v/v)
B.4*c*	FC	85% -52 µm	$FeCl_3.6H_2O$ with 20% HCl (v/v)

Table 1. POSSIBLE ALTERNATIVE METHODS OF CHEMICAL TREATMENT

Material	Stage 1	Stage 2	Subsequent stages
Flotation concentrate (A)	1. Oxidising roast	Acid leach using either	(*a*) 5-10% H_2SO_4 (*b*) Titan effluent (5% H_2SO_4)
	2. Dry grinding to -53 μm	Ferric chloride leach (B)	(*a*) Residue to sulphide volatilisation (*b*) Solution to solvent extraction using perchloroethylene to remove elemental sulphur. (*c*) Residue from (*b*) to (*a*) above or to chloride volatilisation.
	3. Sulphide volatilisation	(*a*) Self sulphiding (*b*) With an excess of elemental sulphur (C)	Treatment as for residues 2 (*a*) and 2 (*c*).
	4. Chloride volatilisation	(*a*) Using chlorine gas (*b*) Using HCl (*c*) Using a metallic chloride (D)	Treatment as for the residue from 2 (*c*).

Notes:
(A) This is at present being sold by Cleveland Tin N.L.
(B) Both the leach and solvent extraction circuits allow regeneration and recycling of leach and solvent liquors respectively.
(C) Excess sulphur (S°) present in the leach residue is about 16 times that necessary to convert the tin present in the leach residue. (Volatilisation with high excess of S° is preferred).
(D) Residual $FeCl_2$ produced by crystallisation from the $FeCl_3$ leach could be used here; spray roasting would regenerate HCl.

Test	*Material*	*Size*	*Solvent*
C.1	FC	100% -52 μm^3	$FeCl_3.6H_2O$ with 20% HCl (v/v)
C.2	FC*	100% -52 μm	$FeCl_3.6H_2O$ with 5% HCl (v/v)
C.3	FC*	100% -52 μm	$FeCl_3.6H_2O$ with 5% HCl (v/v)

* Denotes Sample 713144 used.
† Titan effluent is a waste product from Tioxide Australia Pty Ltd.
[1] RD from roasting flotation concentrate in 'as received' condition.
[2] Concentrate 'as received'.
[3] Concentrate further ground.

A sizing and analysis of the head samples was undertaken, the results of which are outlined in Table 3.

Table 2. LEACH OPERATING CONDITIONS

Test No.	Leach solutions	Mass of FC leached (g)	Volume of leach soln (g)	Temperature (C°)	Time (hr)
A.1*a*	10% H_2SO_4	50	300	room temp.	1
A.1*b*	10% H_2SO_4	50	300	85° ±2°	1
A.2*a*	Titan effluent (50 g/*l* H_2SO_4)	50	300	room temp.	1
A.2*b*	Titan effluent (50 g/*l* H_2SO_4)	50	300	95° ±2°	1
B.1	Titan effluent (50 g/*l* H_2SO_4)	50	150	85° ±2°	2
B.2	1.022 kg $FeCl_3.6H_2O$/*l* of Titan effluent	50	150	104° ±2°	2
B.3*a*	1.022 kg $FeCl_3.6H_2O$/*l* of Titan effluent	50	150	90° ±2°	2
B.3*b*	1.022 kg $FeCl_3.6H_2O$/*l* of 20% HCl (240 g HCl/*l*)	50	150	90° ±2°	2
B.4*a*	1.022 kg $FeCl_3.6H_2O$/*l* of 2% HCl (23 g HCl/*l*)	100	300	104° ±2°	2
B.4*b**	1.022 kg $FeCl_3.6H_2O$/*l* of 5% HCl solution	100	300	104° ±2°	2
B.4*c*	1.022 kg $FeCl_3.6H_2O$/*l* of 20% HCl solution	50	150	104° ±2°	2
C.1 (-45 µm)	1.022 kg $FeCl_3.6H_2O$/*l* of 20% HCl solution	33.33	150	104° ±2°	2
C.2*	1.022 kg $FeCl_3.6H_2O$/*l* of 5% HCl (60 g HCl/*l*)	100	300	104° ±2°	2
C.3	1.022 kg $FeCl_3.6H_2O$/*l* of 5% HCl (60 g HCl/*l*)	100	300	104° ±2°	2

Notes: All slurries were agitated during leaching tests.
* Denotes Sample 713144.

Table 3. SIZING AND ANALYSIS OF HEAD SAMPLE 691183

Fraction #	µm	% Wt	Assay (%)				% Distribution				Cumulative % Distribution			
			C.Sn	S.Sn	T.Sn	Cu	C.Sn	S.Sn	T.Sn	Cu	C.Sn	S.Sn	T.Sn	Cu
+200	+75	5.0	0.27	1.80	2.07	20.6	3.3	3.2	3.2	5.7	3.3	3.2	3.1	5.6
+240	+63	3.5	0.34	1.92	2.26	24.6	2.9	2.3	2.4	4.7	6.2	5.5	5.6	10.4
+300	+53	3.5	0.42	2.26	2.68	24.0	3.6	2.8	2.9	4.6	9.7	8.3	8.5	15.0
+350	+45	5.5	0.53	2.60	3.13	23.0	7.1	5.0	5.3	7.0	16.8	13.4	13.8	22.0
+400	+38	10.1	0.74	2.86	3.60	21.6	18.1	10.2	11.2	12.0	35.0	23.5	25.0	34.0
-400	-38	72.4	0.37	3.00	3.37	16.6	65.0	76.5	75.0	66.0	100.0	100.0	100.0	100.0
Head		100.0	0.42	2.84	3.26	18.0	100.0	100.0	100.0	100.0				

Note: Sample wet screened on 38 µm #

Table 4. RESULTS OF LEACH TESTS

Test No.	Extraction % in filtrate		Residue analysis			Final residue with S°, sulphur removed			S° recovery of that in FC (%)
	% Cu	% S.Sn	% Cu	% S.Sn	% C.Sn	% Cu	% S.Sn	% C.Sn	
A.1*a*	75.8	0.0	9.80	1.10	5.27				
A.1*b*	87.8	17.9	6.30	1.20	6.96				
A.2*a*	71.7	0.0	10.50	1.14	4.55				
A.2*b*	83.9	0.0	7.10	1.40	5.55				
B.1	1.9	0.0	21.00	3.20	0.35				
B.2	72.5	30.6	10.50	3.75	0.76	17.2	6.5	0.98	61.0
B.3*a*	55.5	17.0	17.30	3.90	0.60	23.0	5.6	0.73	43.6
B.3*b*	55.6	17.4	15.70	3.90	0.83	22.3	6.2	0.76	54.6
B.4*a*	69.2	33.3	12.50	3.30	0.71	20.2	5.6	0.91	61.8
B.4*b*	76.7	31.7	8.75	1.00	0.76				
B.4*c*	74.8	34.4	10.00	3.75	0.76	16.2	6.5	1.36	64.0
C.1	85.1	30.8	6.25	4.60	0.92				
C.2	87.5	26.4	3.85	2.30	0.96				
C.3	93.1	17.6	4.38	2.80	0.88	7.3	4.8	1.47	59.3

Table 5. COPPER AND SULPHUR RECOVERY

Product	% Wt	Copper		Soluble Tin		Sulphur		Remarks
		Wt (g)	% Distn	Wt (g)	% Distn	Wt (g)	% Distn	
P/N3 P		16.6	87.8					Cement copper.
P/N3 S/N		0.04	0.2	0.50	25.1			Returned to L1.
L1 S/N		16.64	88.0	0.50	25.1			
L2 S/N		-	-	-	-	21.6	61.7	Elemental sulphur.
L2 R	31.0	2.26	12.0	1.49	74.9	13.4	38.3	Final residue.
L1 R	52.6	2.26	12.0	1.49	74.9	35.0	100.0	
L1 S/N		16.64	88.0	0.50	25.1	-	-	For copper recovery P/N3 P.
L1 R	52.6	2.26	12.0	1.49	74.9	35.0	100.0	For sulphur recovery L2.
Head	100.0	18.90	100.0	1.99	100.0	35.0	100.0	Copper-tin flotation concentrate.

Notes: Operations (1) L1-leaching with ferric chloride 1.022 kg/*l* $FeCl_3 6H_2O$, 58 g/*l* HCl at 104°C.
(2) L2-solvent extraction using carbon disulphide at 20°C.
(3) P/N3-cementation of copper using iron powder.

Products (1) P/N3 P-cement and copper (as Cu metal).
(2) L2 S/N-elemental sulphur.
(3) L2 R-final residue assaying 6.3% Sn, 7.3% Cu, 43.2% S. This contains all the cassiterite tin and about three quarters of the stannite tin.

Analysis of leach products was by atomic absorption spectrophotometer.

In preparing the samples for assay; dilution of the order of 1:100 for tin assay solutions and of 1:1000 for copper assay solutions were required in relation to the weight of sample leached.

Some tin could be volatilised if the leach solution is allowed to boil too vigorously.

LEACH RESULTS

From the leach results (table 4) it can be seen that the ferric chloride leach has some potential. The following points give additional support in favour of a ferric chloride leach.

(1) Apart from the extra grinding of about 12% of the concentrate no further treatment prior to leaching is necessary, *i.e.* both the expense and pollution aspects of roasting are eliminated.

(2) Elemental sulphur of high purity is produced according to the following reaction:

$$CuFeS_2 + 3FeCl_3 \longrightarrow CuCl + 4FeCl_2 + 2S^{\circ}\downarrow$$

(3) The leach is relatively selective; gangue materials, such as pyrite, are not attacked thus accounting for the relatively low recovery of sulphur.

(4) About 90% of the copper is leached out in a single unit in two hours (table 4 and fig. 42).

(5) The leach liquor may be regenerated. Recycling also allows the S.Sn dissolved to be concentrated to a reasonable degree prior to removal after cementation of copper.

TIN, COPPER AND SULPHUR MATERIAL BALANCE

A rough balance showing copper and sulphur recovery is given in Table 5 and Figure 42. Test C.3, which is representative of the optimum reaction conditions for the $FeCl_3.6H_2O$ leach is used as an illustration.

OVERALL FLOW SHEET

The overall ferric chloride leach flow sheet including mother liquor regeneration (fig. 42) is outlined in Table 6.

Table 6. DETAILS OF FERRIC CHLORIDE LEACH (see fig. 42)

Material	Initial stages	Subsequent stages
Flotation concentrate	Dry grinding to -53 µm	
	1. Ferric chloride leach (1)	(*a*) Residue (D) to solvent extraction (A) using perchloroethylene to remove elemental sulphur.
		(*b*) Leach solution cemented with sponge iron (B) at 70°C.
	2. Cementation products	(*a*) Cement copper (2) filtered off prior to (fire) refining.
		(*b*) Mother liquor (6) chlorinated after crystallisation (3) and removal of excess $FeCl_2.4H_2O$.
	3. Recycling of regenerated reagents	(*a*) $FeCl_3.6H_2O$ solution from (*b*) above.
		(*b*) Chlorine by electrolysis (5) of HCl after spray (C) roasting (4) of crystallised $FeCl_2.4H_2O$.
		(*c*) Recovery of perchloroethylene by filtration (E).

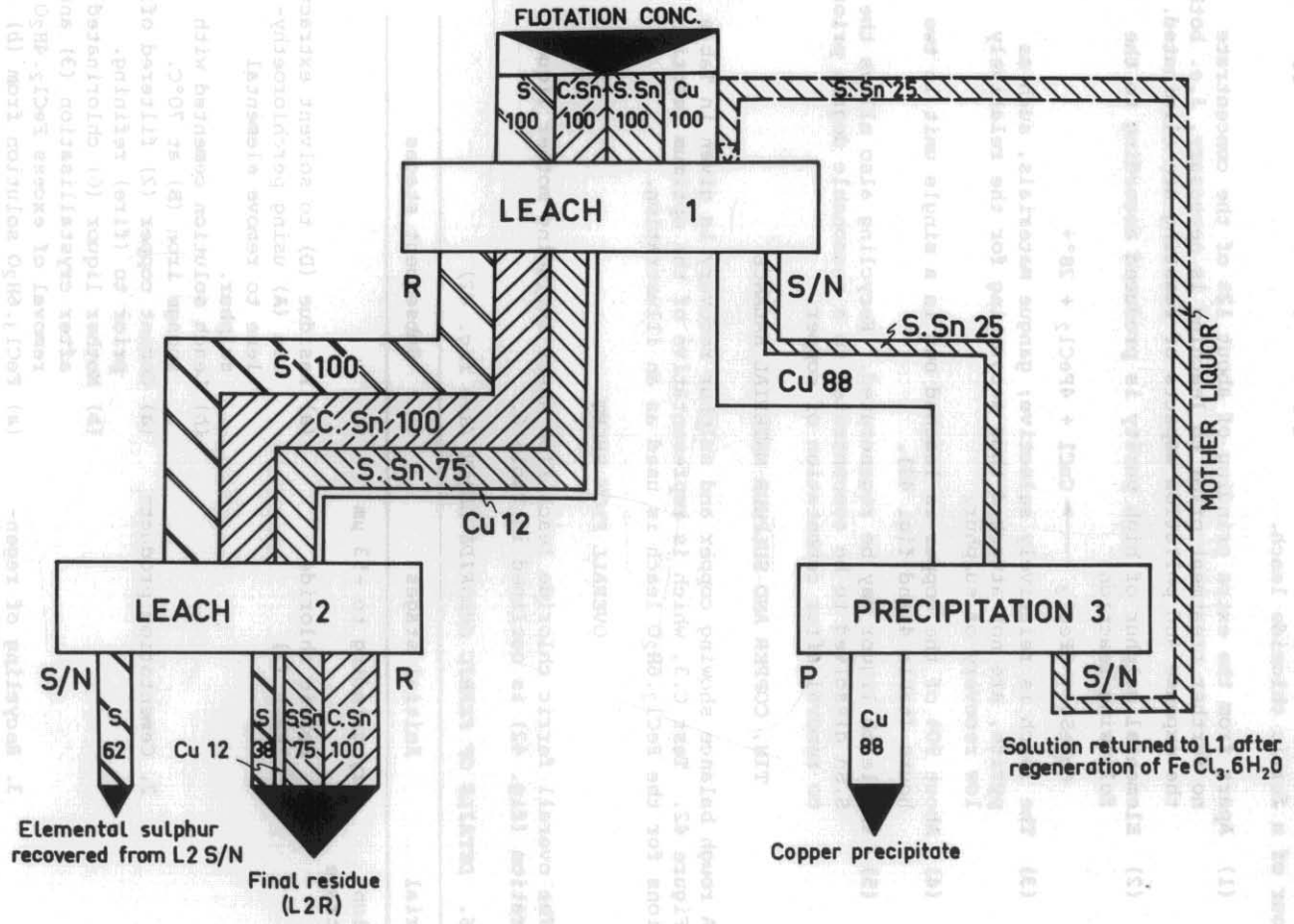

Figure 42. *R.593 Flowsheet showing metal distribution*

Notes on Table 6:

(A) Haver; Wong (1971). Perchloroethylene (P.C.E.) is a desirable solvent for sulphur. P.C.E. is relatively inexpensive, not inflammable, non-toxic, has a high B.P. (121°C) and high density (1625 kg/m^3). The solubility of sulphur in P.C.E. ranges from 25 g/*l* at 25°C to 442 g/*l* at 100°C.

(B) Haver; Wong (1971), Anon (1969), Nadkarni; Wadsworth (1967) and Wadsworth (1969).

(C) Law (1968) and Anon (1971). A by-product disposal problem, besides precluding chlorine and hydrochloric acid recovery, results if ferrous chloride is dumped. Spray roasting eliminates these problems.

(D) Tin could be recovered here by sulphiding with the high excess of sulphur present. (Whitehead, 1962).

(E) Tin recovery by chlorinating with HCl is possible (Whitehead, 1962 and Walden, 1969).

Ferric Chloride Leach and Associated Reactions

(1) $2CuFeS_2 + 6FeCl_3 \longrightarrow 2CuCl + 8FeCl_2 + 4S°\downarrow$

(2) $2CuCl + 8FeCl_2 + Fe \longrightarrow 2Cu + 9FeCl_2$

(3) $9FeCl_2 \xrightarrow{\text{crystallisation}} 6FeCl_2 + 3FeCl_2\downarrow$

(4) $4FeCl_2 + 4H_2O + O_2 \longrightarrow 2Fe_2O_3 + 8HCl$

(5) $8HCl \xrightarrow{\text{electrolysis}} 4H_2 + 4Cl_2$

(6) $6FeCl_2 + 3Cl_2 \longrightarrow 6FeCl_3$

Only reaction (1) is not in commercial use.

OPTIMUM REACTION CONDITIONS FOR THE LEACH

The following conditions, obtained from Haver; Wong (1971) gave the fastest possible rate of reaction.

Time: 2 hours
Particle size of the concentrate: -300#, -52 µm
$FeCl_3/CuFeS_2$ weight ratio: 2.7
Temperature of the solution: B.P. 106°C
Acidity of the leach solution: 5% HCl (60 g/*l* HCl)
Degree of agitation: 100 r.p.m.

The tests were mainly concerned with determining the suitability of a leach solution, and not in investigating the variables controlling the leach. Consequently, only the effects of particle size, HCl concentration and temperature were checked when leaching the flotation concentrate.

The Fe^{3+} concentration employed in the leach tests (212 g/*l*), corresponds to the maximum solubility of the ferrous chloride obtained as a by-product, *i.e.* allows crystallisation of dissolved iron. Because of the obvious advantage of using as concentrated a solution as possible of ferric chloride no investigation as to the effect of Fe^{3+} concentration is necessary.

As anticipated, the above conditions, (where checked) gave the best results as is shown by inspection of Table 4.

'The rate at which the reaction between ferric chloride and chalcopyrite proceeds is of considerable importance, as the retention time in the leaching

operation is directly proportional to the operating volume and hence has a significant bearing on the capital cost of equipment in a large scale operation'. (Haver; Wong, 1971).

CONCLUSION

From the test results obtained using optimum reaction conditions of ferric chloride leach, a plant treating 100 t of concentrate would produce 16 t of copper per day from concentrate containing 18% copper. Besides the copper produced, 22 t of elemental sulphur, 2 t of tin, and a leach solution (to be regenerated) containing about 0.5 t of tin would be obtained.

Notes:

(1) A leach circuit with a capacity of about 27 k*l* would be required.
(2) Such a process would enable the recovery of essentially the same values as smelting without the generation of sulphur oxide gases.
(3) Tests using a regenerated leach solution have not been carried out, otherwise the following may have been verified.

(*a*) The small circulating load of copper remains constant.
(*b*) Progressively less stannite tin may be leached as tin accumulates in the regenerated mother liquor. *i.e.* more tin may end up in the final residue, L2 R of Table 5, on an operating basis.
(*c*) Higher concentrations of tin, than that leached with previously unregenerated ferric chloride, is not cemented with the copper because of the HCl concentration.
(*d*) Stripping of tin from recycled mother liquor may be necessary providing the tin concentration increases sufficiently.

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