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ACID LEACHING OF A SCHEELITE-BEARING ORE FROM CANADA TUNGSTEN MINING CORPORATION LTD., N. W. T., TO REMOVE ACID-SOLUBLE IMPURITIES

by

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EXTRACTION METALLURGY DIVISION

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B.H. Lucas[*] and W.A. Gow[**]

SUMMARY OF RESULTS

A test program has been completed to investigate the possibility of augmenting the recovery of scheelite by flotation, from ore submitted by Canada Tungsten Mining Corporation Ltd., by dissolution of the acid-soluble constituents, mainly dolomite. In the investigation, the leach tests were carried out either on flotation concentrate in order to increase its WO_3 grade, or on flotation feed in order to eliminate the sometimes difficult operation of depressing carbonate minerals which float with the scheelite.

Both dilute hydrochloric acid and aqueous sulphur dioxide solution were effective in decomposing the carbonate minerals present in the samples tested. However, the acid-insoluble mineral contents of the flotation concentrates were too high for the tungsten contents to be increased to the desired 60 - 65% WO_3 merely by leaching out the acid-soluble gangue.

Sufficient sulphur dioxide for leaching the acid-soluble gangue from either scheelite flotation feed or flotation concentrates could be obtained by roasting the pyrrhotite removed from the mine ore in the proposed concentration procedure [1]. Furthermore, roasting of the pyrrhotite would be a source of needed heat. In view of these two factors, and because of the high cost of hydrochloric acid delivered to the remote location of the mine, the sulphur dioxide leach is considerably more attractive economically than a leach process using hydrochloric acid.

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INTRODUCTION

In October 1959, the Mineral Processing Division of the Mines Branch was asked to carry out tungsten concentration tests on a scheelite-bearing ore from the property of Canada Tungsten Mining Corporation Ltd., North West Territory. The results of this investigation were reported in Mines Branch Investigation Report IR 60-80[1]. The recommended procedure for beneficiating this ore, as described in the above report, was the removal of a sulphide concentrate (mainly pyrrhotite) by flotation, followed by tabling of the sulphide flotation tailing for scheelite concentration. The table tailing was then treated by flotation for additional scheelite recovery. The test work showed that about 50% of the tungsten content could be recovered in a table concentrate, at a grade of over 70% WO_3. However, in the subsequent flotation step on the table tailing, it was not feasible to obtain a shipping grade concentrate (60-65% WO_3), if good recovery of the scheelite was to be maintained. The low grade of the scheelite flotation concentrate was attributed, in part, to the dilution of the concentrate by carbonate minerals which could not be depressed preferentially during the scheelite flotation.

Consequently, in October 1960, the Mineral Processing Division asked the Extraction Metallurgy Division to investigate the possibility of upgrading the scheelite flotation concentrate by removing the carbonate minerals by hydrochloric acid leaching. A secondary consideration of the acid treatment program was the

elimination of phosphorus from the scheelite concentrate. Usually there is a penalty against concentrates which contain over 0.1% P_2O_5.

Chemical analyses and a mineralogical study of a typical flotation concentrate indicated that it was diluted both by acid-soluble carbonates and acid-insoluble silicates. The carbonate content was such that the indicated hydrochloric acid requirement for decomposition would be very costly, especially in view of the high transportation cost to this property, while the dilution of the scheelite concentrate by acid-insoluble gangue minerals was such that the desired shipping grade concentrate could not be obtained by dissolution of the acid-soluble gangue.

Although it was necessary to carry out some hydrochloric acid leach tests to confirm these points, it was thought that a more profitable possibility would be to leach out the acid-soluble gangue constituents using an aqueous solution of sulphur dioxide to form soluble bisulphites. Consequently, a test program to investigate this technique was planned. This approach was attractive because the required sulphur dioxide could be obtained at the plant site by roasting the pyrrhotite flotation concentrate which is a by-product in the proposed procedures for recovery of the scheelite. According to Mines Branch Investigation Report IR 60-80, up to 50% of the original ore is pyrrhotite. This pyrrhotite, when concentrated and roasted, would produce sufficient sulphur dioxide for leaching any final or intermediate product from the ore

including sulphide flotation tailing which is equivalent to 50% by weight of the mined ore. In addition the heat produced in roasting the pyrrhotite would be available as plant heat, thus reducing the amount of fuel oil required for the operation of the property.

Assuming that the economics are such that it would be profitable to roast as much of the pyrrhotite as required, several possibilities for using the sulphur dioxide leach become apparent. It might be desirable to leach the acid-soluble gangue out of the pyrrhotite flotation tailings so that it would not be necessary to resort to difficult preferential carbonate depression during subsequent scheelite flotation. Another possibility is to produce a rougher scheelite-carbonate mineral flotation concentrate from which the carbonate mineral could be leached with sulphur dioxide. The leached scheelite-bearing residue could then be re-treated by flotation to eliminate the acid-insoluble content.

Although it is common practice in the treatment of scheelite mineral concentrates to use hydrochloric acid to remove carbonate impurities[2], sulphur dioxide has not been used for this purpose. However, sulphur dioxide is used extensively in the pulp and paper industry to produce soluble calcium bisulphite from limestone[3] and it was hoped that an adaptation of the techniques used in the pulp and paper industry (Appendix A) could be applied to this problem.

In order to investigate these possibilities, sulphur dioxide leach tests were done on scheelite flotation feed and on scheelite flotation concentrates containing various concentrations of acid-soluble minerals.

EXPERIMENTAL PROCEDURE

Description of Samples

The samples of feed product used in this investigation were all supplied by the Mineral Processing Division and could be classified broadly into two types: scheelite-bearing flotation concentrate, and tungsten ore from which the sulphides and some of the scheelite had been removed by flotation, and gravity methods, respectively (scheelite flotation feed).

Three different scheelite-bearing flotation concentrates were supplied (Table 1). The concentrate having the highest tungsten content, 46.2% WO_3, was a product of the pilot plant testing described in Mines Branch Investigation Report IR 60-80. The other two scheelite-bearing flotation concentrates were produced in small scale batch tests, No. 7 and No. 24. The procedure followed in making the latter two concentrates was similar, generally, to that used in the pilot plant operation mentioned. Table 1 shows the results of chemical analyses done on all three scheelite-bearing flotation concentrates.

TABLE 1

Chemical Analysis of Scheelite-bearing Flotation Concentrates

(%)

Analysed for	Sample from Pilot Plant	Sample from Batch Test No. 7*	Sample from Batch Test No. 24*
WO_3	46.2	23.8	18.5
CaO	16.8	28.3	---
CO_2 (evolution)	1.56	16.3	8.2
CO_2 (combustion)	2.52	--	--
Fe Total	4.30	--	--
S Total	1.06	--	--
P_2O_5	1.27	--	--

*Mineral Processing Division Test Numbers

The sample of scheelite flotation feed was produced by the Mineral Processing Division to simulate ore material which would be leached by aqueous sulphur dioxide solution, utilizing SO_2 produced from the roasting of the sulphides. The sample was designated as sample No. 18 by the Mineral Processing Division. Table 2 shows the results of the chemical analysis of the sample. The method of producing the sample included grinding to minus 80 mesh, floating off the sulphides, tabling the sulphide tailings to remove a high grade scheelite concentrate, and retaining the table tailings for leach treatment.

TABLE 2

Chemical Analysis of Scheelite Flotation Feed

(%)

Analysed for	Sample No. 18*
WO_3	0.55
CaO	13.5
CO_2 (evolution)	1.30
CO_2 (combustion)	2.54
Fe Total	11.6
S Total	1.82
P_2O_5	0.09

*Mineral Processing Division Test Number

The results of a mineralogical investigation of the mine ore were as follows:

"The ore is a coarse-to fine-grained quartz-pyroxene rock containing up to 50% sulphide mineral of which up to 2% is chalcopyrite and the remainder is pyrrhotite. The only tungsten mineral is scheelite which occurs as disseminated grains, in the minus 65 plus 325 mesh range. In addition to the quartz and pyroxene, other gangue minerals present are feldspar, dolomite, biotite and clay types[4]."

Table 3 shows the approximate mineralogical compositions, estimated from chemical analyses and mineralogical observations, of two products submitted for leaching.

TABLE 3

Estimated[*] Mineral Composition of Leach Feeds
(%)

	Scheelite Concentrate from Pilot Plant[**]	Scheelite Flotation Feed [**] (Sample No. 18)
Scheelite	57	0.7
Limestone	6	3
Pyrrhotite	2	5
Apatite	3	0.1
Pyroxene	26	20
Other gangue minerals (by diff.)	6	71.2
	100	100

(Limestone, Pyrrhotite, Apatite bracketed together marked [***])

[*] These estimations are made on the assumptions that all the sulphur is present as pyrrhotite (FeS), that the CO_2 determined by evolution is present as $CaCO_3$, and that the pyroxene contains 15% Fe and accounts for the remainder of the iron not accounted in the pyrrhotite.

[**] Chemical analyses of these samples are shown in Tables 1 and 2.

[***] Minerals which are soluble in dilute HCl solution.

Laboratory Test Work

The laboratory test work consisted of two series of bench scale leach tests. In one series of tests hydrochloric acid, and in the other series sulphur dioxide, was added to an aqueous slurry of

the feed sample which was mechanically agitated in a beaker. The success of the leaching technique was assessed by analysing the leach feed, leach residue and leach solution samples for WO_3, CO_2 (present as carbonate), CaO, P_2O_5 and Fe, as applicable.

The hydrochloric acid leach tests were done on samples of scheelite-bearing flotation concentrate to check some of the more obvious variables, and to confirm the indication that hydrochloric acid leaching would be neither economical nor effective. In all, six hydrochloric acid leaches were carried out on the two higher grade scheelite-bearing flotation concentrates shown in Table 1. The conditions used in these tests were chosen to give some indication as to effects of temperature, pulp density and acidity. Concentrated hydrochloric acid (37.5% HCl), was added to the aqueous slurry to give a moderately intensive attack on the dolomite gangue content, at uniform pH levels, in the 0.4 to 1.0 range. The pH was measured by means of pH meter[*], the electrodes of which were submerged in the slurry throughout the test. In these tests, leaching times of 1 1/2 to 3 hours, pulp densities of 50 to 67% solids, and pulp temperatures of 20 to 70°C, were investigated.

In the first five of the hydrochloric acid leach tests the leached residue was separated from the leach solution by two stages of decantation and one of repulping. After the second decanting, hydrochloric

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[*] Beckman Zeromatic laboratory pH meter

acid was again added for a second stage of leaching in an attempt to lower the P_2O_5 content, since dissolution of apatite in the first stage is inhibited by the calcium chloride formed[2]. In all tests, Aerosol OT was added to the first stage leach, prior to the acid addition, to improve the hydrophilic characteristics of the mineral surfaces previously coated with flotation reagents. The amounts of Aerosol OT used were 0.03 to 0.05 lb/ton.

Sulphur dioxide leach tests were carried out on samples of both scheelite-bearing flotation concentrate and scheelite flotation feed. In most of these tests, a 10% SO_2 - 90% nitrogen mixture was fed to the mechanically agitated aqueous slurry of ore through a fritted glass sparger (in the small scale tests) or through a tube containing four 1/16" dia holes (in the larger scale tests). The 10% SO_2 - 90% nitrogen mixture was chosen to simulate the SO_2 concentration of roaster gas. The SO_2 flow control was based on continuous weighing of the SO_2 cylinder, while the nitrogen flow rate was metered by means of a rotameter. The rate at which the gas mixture was fed ranged from 5 to 120 g SO_2/hr. In two of the tests, the SO_2 concentration in the gas mixture was increased from the usual 10% SO_2 to 24 and 36% SO_2. The pulp densities in these tests varied from 23 to 38% solids. In one test the leaching was done in two stages. Washing of the leached residue was accomplished using first a concentrated aqueous solution of SO_2, followed by water. The progress of the leach was followed by utilizing iodine or iodate and sodium hydroxide titrations to determine the free and total SO_2 present in the leach liquor (Appendix B).

RESULTS

The results obtained from the leaching of various scheelite-bearing flotation concentrates with dilute hydrochloric acid are shown, along with the test conditions utilized in each test, in Table 4. It should be noted that the hydrochloric acid consumption data given in Table 4 are in terms of 100% HCl.

The results of leaching both scheelite-bearing flotation concentrates and scheelite flotation feeds with aqueous solutions of sulphur dioxide, along with the test conditions utilized, are shown in Table 5.

Figure 1 shows the rate of dissolution of the carbonate minerals, during a sulphur dioxide leach (Test 806), by the increase in the CaO content of the leach liquor and by the decrease in the CO_2 (by evolution) content of the leach residue.

DISCUSSION

The estimated mineral composition of the pilot plant scheelite concentrate submitted showed that only about 11% of the product was composed of minerals which would be soluble in dilute acid solution (Table 3). This amount of acid-soluble gangue was not sufficient to permit upgrading of the concentrate to the required 65% WO_3 grade by acid leaching. These indications were confirmed by the results of the HCl leach tests done on the pilot plant concentrate, which showed

TABLE 4

Hydrochloric Acid Leach Tests on Scheelite-bearing Flotation Concentrates

Test No.	Feed	Stage No.	Pulp Density (% solids)	Temp (°C)	Final pH	Acid Consumption (lb/ton)	Ret. Time (hr)	Product	Wt (g)	Vol (ml)	pH	Wt Loss (%)	WO₃ Soluble Loss (%)	WO₃	CO₂	CaO	P₂O₅	WO₃	CaO	P₂O₅
														Analyses (%, g/l)				Distribution (%)		
F	Scheelite concentrate from pilot plant flotation. (Table 1)	1	50	20	1.0	78.1	1.5	Feed	100					46.7	1.56(a)	16.9	1.31	100.0	100.0	100.0
		2	50	20	0.5	62.0	1.5	Final residue	92.1			7.9	} 0.2	50.6	0.2	15.0	0.01	99.8	81.8	0.8
		Total				140.1	3.0	1st stage leach liquor		79	1.3			0.23		20.4	6.81	} 0.2	18.2	41.2
								2nd stage leach liquor		72	0.5			0.44		10.4	6.24			34.4
								1st stage wash liquor		77				0.03		5.1	1.30			7.6
								2nd stage wash liquor		419				0.03		0.8	0.49			16.0
G	"	1	50	50	1.0	94.6	1.5	Feed	100					48.4	1.56(a)	17.3	1.41	100.0	100.0	100.0
		2	50	50	0.7	91.6	1.5	Final residue	90.6			9.4	} 0.40	53.2	0.03	15.2	0.014	99.6	79.7	0.8
		Total				186.2	3.0	1st stage leach liquor		65	1.2			0.08		25.3	6.24	} 0.40	20.3	28.7
								2nd stage leach liquor		68	0.8			1.36		13.7	8.58			41.8
								1st stage wash liquor		71				0.02		6.64	1.5			7.7
								2nd stage wash liquor		492				0.20		0.95	0.62			21.6
H	"	1	50	70	1.0	101.4	1.5	Feed	100					47.2	1.56(a)	16.8(a)	1.16	100.0	100.0	100.0
		2	50	70	0.7	97.5	1.5	Final residue	87.2			12.8	} 3.3	52.4	0.14	15.1	0.01	96.7	77.9	0.8
		Total				198.9	3.0	1st stage comb. liquor		136	1.7			0.24		2.59		} 3.3	22.1	31.7
								2nd stage leach liquor		74	0.7			12.55		7.35				45.7
								2nd stage wash liquor		412				1.42		0.63				21.8
L	"	1	67	70	0.4	190.0	4	Feed	1500					44.7				100.0		
		2	67	60	1.0	4.0	1	Final residue	1336			10.9	} 0.9	49.7				99.1		
		Total				194.0	5	1st stage leach liquor		340	0.4			2.13				} 0.9		
								2nd stage leach liquor		257	1.1			4.57						
								1st stage wash liquor		462				0.75						
								2nd stage wash liquor		3290				1.09						
N	"	1	50	55	0.8	100.0	2.0	Feed	1426					44.7		16.8(a)	1.27(a)	100.0	100.0	100.0
		2	50	55	0.8	66.4	1.0	1st stage residue	-					48.7		17.1	0.54	99.9		
		Total				166.4	3.0	2nd stage residue	1289			9.7		49.4		15.8	0.01		64.6	0.7
M	Scheelite concentrate from batch test No. 7 (Table 1)	1	50	60	1.0	910.0	1.5	Feed	50					20.6	16.3(a)	28.3(a)		100.0	100.0	
								Final residue	20.5			59.0	} 0.2	50.2		28.1	4.59	99.8	42.3	
								Leach liquor		90	0.7			0.05				} 0.2	57.7	
								Wash liquor		318	4.4			0.03						

Note: 1. Feed analyses marked (a) are analyses taken from Table 1; all other feed analyses are calculated from analyses of products.
2. In Test G, 0.05 lb Aerosol OT used in leach, and in Test N, 0.03 lb Aerosol OT was used.

O-CaO   IN LEACH LIQUOR BY CHEMICAL ANALYSIS

⊖-CaO   AS CALCIUM BISULPHITE FROM TEST CONTROL
          ANALYSIS OF LIQUOR

⊕-RESIDUAL CO_2 IN RESIDUE

CaO ANALYSIS OF LEACH LIQUOR, G/L

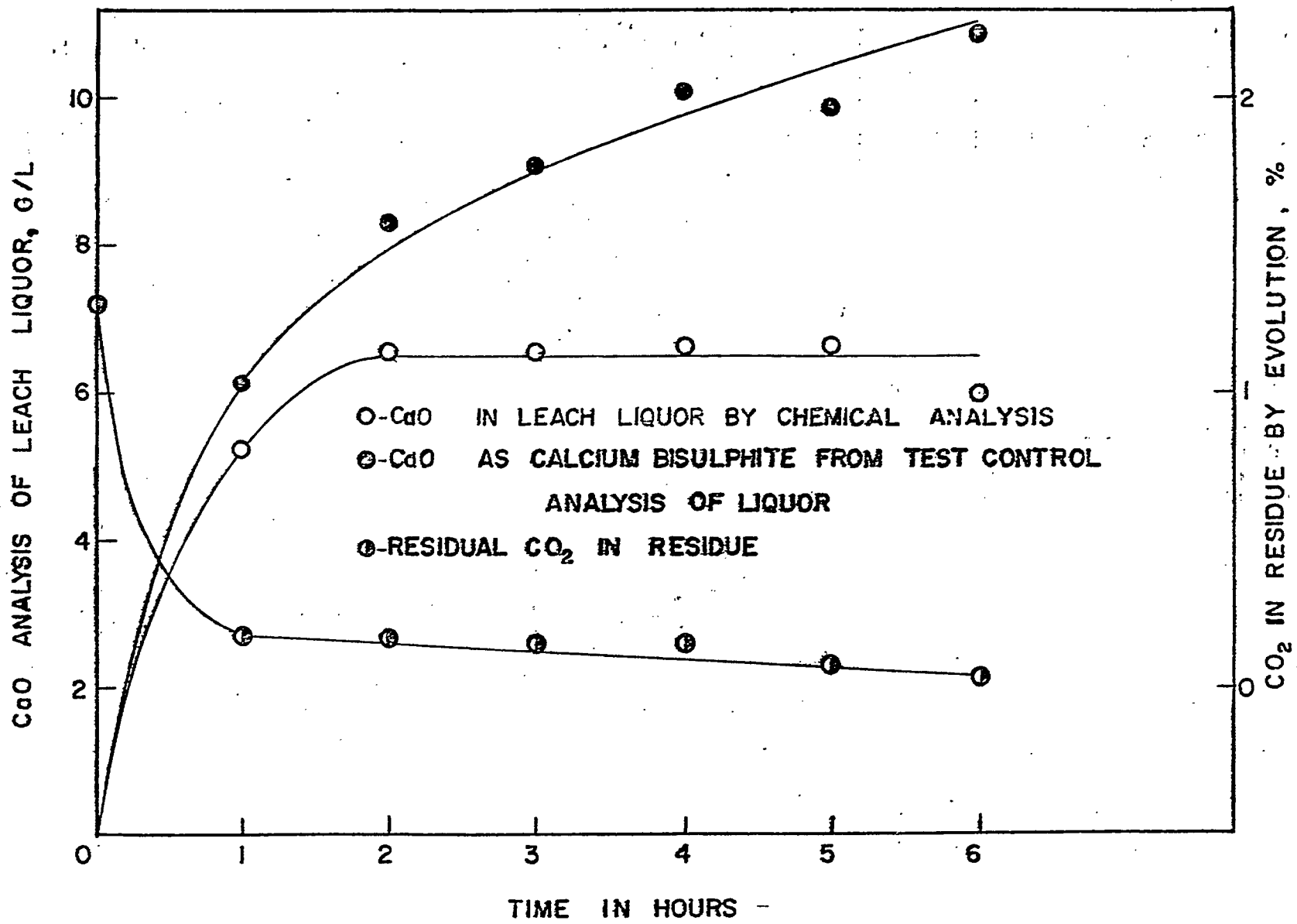CO_2 IN RESIDUE BY EVOLUTION , %

TIME IN HOURS –

FIGURE I. LEACH RESULTS OF TEST 806

that the weight loss in acid treatment varied between 7.9 and 12.8%,
and the acid leach residue analysed from 49.4 to 53.2% WO_3 (Table 4).
It is obvious then that if a leach residue containing 60 - 65% WO_3 is to
be obtained, the flotation concentrate must contain only a small
amount of insoluble gangue, and also, if the hydrochloric acid consump-
tion is to be kept within economic limits, the acid-soluble gangue must
be kept to a minimum; probably not more than about 5% by weight.
However, if it is not possible to meet these two conditions it might
be feasible to re-float the scheelite from these leach residues to
produce the desired WO_3 grade since, after leaching, the acid-
soluble gangue would not be present to complicate the flotation
procedure.

If hydrochloric acid leaching of a flotation concentrate is
worthy of consideration in the processing of this ore, the results
shown in Table 4 indicate some of the factors to be considered. The
acid concentration of the leach solution does not have to be higher
than that required to give a pH value of 1.0. The solid weight loss
due to dissolution of the acid-soluble minerals is increased with
leaching temperature. However, the temperature should not exceed
60°C, at least at pH 1.0, if the amount of tungsten lost by dissolution
is to be kept at a minimum. This is shown by the high tungsten loss
in Test H. In order to lower the P_2O_5 to below the specified maximum
content, a second stage HCl leach is necessary. This is indicated
by Tests F, G, and H where 35 - 45% of the dissolved P_2O_5 reports in

the second stage leach liquors, and by Test N, where the P_2O_5 content of the first stage residue is 0.54% P_2O_5 after leaching 2 hours, but the second stage residue contains only 0.01% P_2O_5 after 1 additional hour. For a concentrate containing about 1.5% CO_2 as carbonate mineral, the acid consumption would be between 175 - 200 lb 100% HCl/ton of concentrate, as shown by Tests G, H, L and N. In Test M where the CO_2 content as carbonate was 16.3%, the acid consumption was 910 lb 100% HCl/ton of concentrate; an economically prohibitive amount.

The leaching of scheelite ore or flotation concentrate similar to the samples submitted, using an aqueous sulphur dioxide solution, appeared to be a feasible procedure, as shown by the results given in Table 5.

From both a low grade tungsten rougher concentrate, as represented by the leach feed in Test 812, and a scheelite flotation feed, as represented by the feed in Tests 801 - 806, a 10% SO_2 - 90%N gas mixture fed to an aqueous slurry of the leach feed at 23 - 38% solids at ambient room temperatures eliminated most of the carbonate content, as indicated by the CO_2 analyses of the leach residue, in 4 hr leach time or less. Figure 1 shows that, with scheelite flotation feed, the acid-soluble calcium in the leach feed is dissolved in less than 2 hr. The data in Table 5 show that not more than 40 lb SO_2/hr/ton of leach feed is required for successful leaching of the soluble gangue

TABLE 5

SO₂ Leaching of Scheelite-bearing Flotation Products

Test No.	Feed	Nominal Leach Conditions					Product	Wt (g)	Vol (ml)	Final (pH)	Wt loss (% of feed)	Analyses *(% or g/l)				Comments
		Pulp density (% solids)	Ret. time (hr)	SO₂ Rate (g/hr)	Rate (lb/hr/ton)	% conc. in nitrogen						WO_3	CO_2 (evol)	CaO	Fe	
812	Scheelite-bearing flotation concentrate (Batch Test 24, Table 1)	33	4	40	115	10	Feed	649				18.5	8.2			Leaching done in two stages with decanting and repulping between stages.
		33	4	40	115	10	Final residue	492			24.2	24.4 (calc)				
801	Scheelite flotation feed (Sample 18, Table 2)	23	6	20	133	10	Feed	300				0.55	1.30	13.5	11.6	
							Final residue	272		1.6	9.3		0.02			
804	"	23	3	40	266	10	Feed	300				0.55	1.30	13.5	11.6	.
							Final residue	279		1.8	7.0		0.06			
805	"	23	4	40	266	10	Feed	300				0.55	1.30	13.5	11.6	
							Final residue	282		2.1	6.0		0.04			
802	"	23	2	120	798	36	Feed	300				0.55	1.30	13.5	11.6	
							Final residue	277		1.6	7.7		0.06			
803	"	38	6	60	399	24	Feed	300				0.55	1.30	13.5	11.6	
							Final residue	272		1.9	9.3		0.04			
806	"	31	6	60	38.6	10	Feed	3115				0.55	1.30	13.5	11.6	Figure 1 shows extraction rate curves. Other analyses on the leach liquor were P_2O_5-0.002 g/l and MgO - 0.10 g/l. Residue P_2O_5 = 0.04%
							Final residue	2920			6.3	0.59	0.04	12.9	10.7	
							Leach liquor		5980	2.8		0.003		5.93	5.99	
							Wash liquor		3830					1.84	1.09	

* In order to conserve leached product for subsequent flotation test work only a minimum of analyses was done.

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minerals from scheelite flotation feed (Test 806). For a 2 hr leach time this would amount to only 80 lb SO_2/ton of leach feed; less than 10% of the SO_2 which could be available from roasting all the sulphide in the mine ore. Because of the small scale of most of the leach tests, it was not practicable to feed the SO_2 to the test at a rate less than 20 g/hr. The SO_2 feed rate was high in most of the tests shown in Table 5 and varied from 115 lb SO_2/hr/ton leach feed in Test 812 to 798 lb SO_2/hr/ton leach feed in Test 802. However, the high rate of SO_2 addition in the latter test would have had little effect since the excess would not have been taken into solution. In these tests on scheelite flotation feed, the variations in weight loss may have been due to minor attack on other minerals since analyses in one test showed iron in solution, but possible experimental variations of the small scale test work preclude any definite conclusions.

In Test 812, the solids weight loss of 24.2% indicates that the sulphur dioxide leach was successful in dissolving the acid-soluble gangue from scheelite-bearing flotation concentrate. Two stages of leaching were done in this test to be sure that maximum gangue dissolution had been accomplished.

The phosphate-bearing minerals are only slightly attacked by the sulphur dioxide leach and if, in addition to removing the acid-soluble gangue from the scheelite flotation concentrate, it were required to lower the P_2O_5 content to meet specifications, retreatment

by the normal hydrochloric acid leach procedure[2] would be necessary. To save transportation costs this could probably be done at a point closer to the source of hydrochloric acid. Hydrochloric acid requirements should be small after the soluble gangue has been removed by sulphur dioxide leaching.

The rather more complete analyses carried out on the products from Test 806 indicate that the tungsten losses during leaching are small; the leach liquor contained only 0.003 g WO_3/l. The indications are that the tungsten loss would be less if a SO_2 leach were used rather than an HCl leach. The P_2O_5 analysis on the leach liquor confirms the fact that the SO_2 leach does not dissolve the phosphate minerals.

If a procedure involving the dissolution of the acid-soluble minerals from scheelite flotation feed with sulphur dioxide leach solution were contemplated, some further work should be done on the washing and neutralizing of the SO_2 leached residue to prepare it for subsequent flotation. In the test work done, in order to remove all the residual soluble salts from the SO_2 leached residue prior to flotation, the residue, after primary filtering, was washed with strong SO_2 solution (50-75 g SO_2/l), followed by repulping in cold water and filtering several times to reduce its acidity. This technique probably would not be satisfactory in practice since even after using a volume of cold water equivalent to 1-2 gal/lb solids in washing, the repulped

solids still retained a pH value of about 5. It would probably be

necessary to neutralize the residual acidity chemically with soda ash

or caustic. It is recognized that such a neutralizing procedure might

interfere with subsequent flotation since it would result in precipita-

tion of iron which, as indicated in the results of Test 806, Table 5,

is present in the leach and wash solutions from the SO_2 leach.

Figure 1 indicates that the analytical method used in the labo-

ratory to follow the dissolution of the gangue mineral as bisulphite

(Appendix B) showed a higher concentration of calcium in the leach

liquor than was actually present. The reasons for this were not

investigated since it appeared that, on the samples leached, careful

control of the ratio of the bisulphite to total SO_2 in solution was not

necessary for satisfactory leaching. If such a control was thought

to be necessary, the analytical procedure would require modification.

CONCLUSIONS

The acid-soluble gangue in these tungsten ore products can be

removed either by conventional hydrochloric acid leach, or by

leaching with aqueous sulphur dioxide solution.

The hydrochloric acid treatment removes both the acid-soluble

gangue and the phosphorus minerals, but some loss of tungsten is

indicated. The hydrochloric acid would have to be transported to the

mine site at some extra cost.

The sulphur dioxide solution treatment removes the acid-soluble gangue but there is no attack on the phosphorus minerals. Mineralogical examination and analyses show that there is more than adequate sulphide content in the ore to supply the necessary sulphur dioxide, and the roasting of the sulphides could be a useful source of heat for the property. If the phosphorus is a problem, the leached products may be re-treated, with low hydrochloric acid requirement, closer to the source of hydrochloric acid.

ACKNOWLEDGMENTS

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APPENDIX A

Visit to the E. B. Eddy Pulp Mill, Hull, Quebec

A visit was paid to Mr. J. H. Feiner, of the E. B. Eddy Company, to obtain some information in the production of soluble calcium bisulphite by treating limestone with sulphur dioxide. The following points were discussed:

1) The control analysis procedure was detailed. (See Appendix B).

2) High calcium limestone dissolves readily in sulphur dioxide solutions. Dolomitic limestone cannot be used in a tower method because of its inertness, but lime produced from dolomite reacts readily.

3) Soluble calcium bisulphite $Ca(HSO_3)_2$ forms in an excess of SO_2 which must be maintained. The $Ca(HSO_3)_2$ is more stable in cold water. If calcium sulphite precipitates, it can be redissolved by the addition of excess SO_2.

4) Pulp mills burn sulphur, but have also roasted sulphides to produce SO_2 at approximately 10% concentration. The gas must be cooled down quickly through the SO_3 formation range. Cooling is by spray tower which will scrub out SO_3, and also stop SO_3 formation. Residual oxygen in the SO_2 gas does not interfere with $Ca(HSO_3)_2$ formation or solubility.

5) The Kimberley Clark Co. at Kapuskasing, Ontario, have designed and operate a bubble plate tower for handling limestone slurries.

6) Dr. N. Katz, formerly of the National Research Council, did considerable research on atmospheric SO_2 dispersion for Consolidated Mining and Smelting Co., Trail, B.C. with respect to air pollution problems.

APPENDIX B

SO_2 Control Analysis Method

1. Add 1 ml liquor to 25 - 50 ml water.

2. Add a few drops of methyl orange indicator, and 4 ml potassium iodide solution and starch.

3. Titrate with 1/8 N potassium iodate solution (found to be better and simpler than iodine).

4. Add a few drops of potassium thiosulphate to get rid of blue end point.

5. Titrate with 1/8N sodium hydroxide.

Calculations

$$\text{Free } SO_2 = \text{Vol } KIO_3 \times \text{factor} \quad g/l$$

$$\text{Total } SO_2 = \text{Vol NaOH} \times \text{factor} \quad g/l$$

$$\text{Factor} = \frac{N \text{ of titrating solution} \times \text{eq wt } SO_2}{\text{vol of liquor sample}}$$

Total SO_2 includes the free SO_2 plus one half of the combined SO_2 in the $Ca(HSO_3)_2$, therefore SO_2 present as calcium bisulphite

$$= 2(\text{total } SO_2 - \text{free } SO_2)$$

Example of Typical Calculation

$$
\begin{aligned}
&\text{(1)} \quad \text{Volume leach liquor} \;=\; 1 \text{ ml} \\
&\text{(2)} \quad \text{Normality of KIO}_3 \;=\; 0.098 \\
&\text{(3)} \quad \text{Normality of NaOH} \;=\; 0.099 \\
&\text{(4)} \quad \text{Equivalent wt SO}_2 \;=\; 32 \\
&\text{(5)} \quad \text{Titrations: Iodate} \;=\; 6.02 \text{ cc} \\
&\qquad\qquad\qquad\quad\; \text{NaOH} \;=\; 8.98 \text{ cc}
\end{aligned}
$$

$$\therefore \text{ free SO}_2 = 6.02 \times \boxed{\frac{0.098 \times 32}{1}} = 18.88 \text{ g/l}$$

$$\text{Total SO}_2 = 8.98 \times \boxed{\frac{0.099 \times 32}{1}} = 28.45 \text{ g/l}$$

$$\text{SO}_2 \text{ as calcium bisulphite} = 2\,(28.45 - 18.88) = 19.14 \text{ g/l}$$

$$\text{CaO as calcium bisulphite} = 19.14 \times \frac{\text{Ca(HSO}_3)_2 \times \text{CaO}}{2\,(\text{SO}_2) \times \text{Ca(HSO}_3)_2}$$

$$= 19.14 \times \frac{56.1}{128.2} = 8.38 \text{ g/l}$$

and CaO by analytical laboratory $= 8.20 \text{ g/l}$