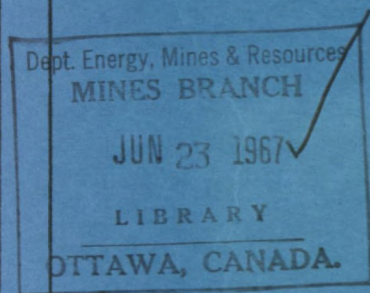




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MINES BRANCH
OTTAWA

*A PROCESS FOR PREPARING TUNGSTIC
TRIOXIDE OF HIGH PURITY
FROM A CANADIAN SCHEELITE
CONCENTRATE*



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EXTRACTION METALLURGY DIVISION

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A Process for Preparing Tungstic Trioxide of High Purity from a Canadian Scheelite Concentrate

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ABSTRACT

A new process for treating scheelite for the production of tungstic trioxide is described. The novelty of the process resides in that an ion-exchanger is used to convert sodium tungstate to either ammonium tungstate or tungstic acid.

The process consists of a conventional hydrochloric acid leach of the scheelite concentrate, and the dissolution of the impure tungstic acid thus produced with sodium hydroxide at pH 8. The sodium tungstate solution is clarified and passed through a column of Dowex 50Wx8 ion-exchange resin to exchange the sodium ions for either hydrogen or ammonium ions, both being suitable. The tungsten-bearing column effluent is evaporated to crystallize the tungsten as ammonium tungstate; the crystals are washed with nitric acid and water and decomposed by heat to produce tungstic trioxide of high purity.

Ninety-six per cent of the tungsten in the concentrate may be recovered as tungstic trioxide (WO_3), and the reagents consumed are 0.7 g HCl, 0.41 g NaOH and either 1.73 g NH_4Cl or 225 g HCl per gram of tungsten.

soluble residue from the acid leach, is then dissolved with ammonia and reprecipitated by acid neutralization or evaporation to produce ammonium paratungstate. To obtain the desired purity of 99.95 per cent WO_3 in the final product, the tungstate may have to be dissolved and precipitated repeatedly. The literature also describes processes in which the scheelite is decomposed with alkali (2), and reference is made to a process in which liquid-liquid extraction is used to remove molybdenum and other undesirable impurities (2).

The scheelite concentrate used in this work was kindly supplied to us by Canada Tungsten Mining Corporation Limited. On the basis of its composition, it appeared that it would most likely respond to treatment by the well-described conventional methods.

However, the leaching of tungstic acid by ammonia, as is done in the conventional method, is difficult to control and cumbersome if several dissolution and crystallization steps are necessary for purification. Consequently, it was thought that dissolution of the tungstic acid could be more easily done using sodium hydroxide instead of ammonia, and that tungstic trioxide could be produced from the sodium tungstate solution by an ion-exchange technique.

The application of an ion-exchange technique to the preparation of pure tungstic trioxide from scheelite appealed to us for three reasons: first, it was thought that an ion-exchange process would be easier to control than a recrystallization process; second, an ion-exchange process offered the possibility of converting tungsten compounds from sodium tungstate to tungstic acid or ammonium tungstate; and, third, an ion-exchanger might selectively adsorb undesirable impurities from tungsten-bearing solutions, thus effect-

ing a purification of the tungsten products.

The conditions for decomposing the scheelite concentrate, which contained 71.3 per cent WO_3 , using either hydrochloric acid or sodium hydroxide were established. Where the scheelite was decomposed with hydrochloric acid, the dissolution of the tungstic acid with sodium hydroxide followed by conversion of the sodium tungstate to ammonium tungstate or tungstic acid by ion-exchange processing was investigated. Finally, results obtained by this technique were compared with those obtained by treating the scheelite concentrate by the conventional process.

Procedure

The scheelite concentrate used in the investigation, produced by Canada Tungsten Mining Corporation Limited, contained 71.3 per cent WO_3 (83.6 per cent $CaWO_4$). An analysis of the concentrate by chemical and semi-quantitative spectrographic methods is reported in Table I. The impurities which were analysed by chemical methods are indicated by asterisks.

The acid leach tests were carried out in a glass reaction vessel heated by means of an electric mantle. During leaching, the slurry was agitated vigorously using a mechanical stirrer to keep the dense concentrate in suspension. The alkali leaching of the crude tungstic acid produced by acid leaching was done in a Teflon beaker, also heated by a mantle. In this step, the use of glassware in contact with the leach solution was avoided to eliminate the possibility of silica contamination in the final product. The solid-liquid separations were made by filtration through laboratory filter paper, using a Buchner funnel. The sodium tungstate solutions fed to the ion-exchange column were clarified by filtering them through

Introduction

THE recent development of a major tungsten-producing mine in Canada led us to take an interest in new methods for producing high-purity tungsten compounds from Canadian raw materials in the hope that our work may lead to the production of tungsten compounds and of tungsten metal in Canada.

The technology of extracting tungsten from scheelite is well described in the literature (1, 2), and a method conventionally used consists of leaching scheelite, previously concentrated, with hydrochloric acid to remove the easily soluble impurities and dissolve the calcium. The resulting crude tungstic acid, which remains as an in-

Table I—Analysis of Scheelite Concentrate

Element	%	Element	%	Element	%
Ag	0.0001	Mn	0.4	SiO ₂	3.7*
Ba	0.03	Mo	0.011*	Sr	trace
Be	0.0001	Na	trace	Ti	0.03
Bi	0.017*	Ni	0.008	V	trace
Al	0.4	P	0.05*	WO ₃	71.3
CaO	18.98*	Pb	trace	Yb	0.007
Cu	0.001	As	<0.01*	Y	0.03
Fe	1.75*	S	0.26*	Zr	0.01
Mg	0.3	Sn	trace		

Table II—Results Obtained by the Conventional HCl-NH₃ Method for Treating the Scheelite Concentrate

Acid Leaching g HCl/g W	Ammonia Leaching of Crude H ₂ WO ₄	
	58% NH ₃ OH g NH ₃ /g W	Tungsten Extracted per cent
0.7	0.5	80

Table III—Analysis of Tungstic Anhydride Produced by Conventional HCl-NH₃ Method

W	Al	As	Bi	CaO	Cu	Fe	Mg	Mn	Na	P	S	Si
%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
77.1	<1	<50	<50	<200	0.4	<50	<0.1	<0.1	<1	<100	<100	22

a bed of cellulose filter medium.

The tests with the ion-exchange resin were carried out by passing the feed solutions through a glass column, 48 cm high and 3 cm in diameter, containing 200 ml of wet, settled Dowex 50Wx8 cation-exchange resin. The tungsten-bearing column effluents were evaporated in a Teflon beaker, but not to dryness. The tungsten crystals were washed with nitric acid and water, filtered and heated at a temperature of between 500 and 600°C in a platinum crucible. The tungstic trioxide produced was analysed by spectrographic, chemical and X-ray diffraction methods.

Results

A first test was carried out to evaluate the efficiency of the conventional hydrochloric acid - ammonia method to extract the tungsten from the scheelite concentrate, and to evaluate the chemical quality of the tungstic trioxide produced using a one-step crystallization process. The concentrate was agitated for 3 hours at 100°C in 37 per cent hydrochloric acid. The residue was washed with acidified water, filtered and agitated at room temperature in 58 per cent ammonium hydroxide solution for 3 hours. The specific gravity of the filtrate was adjusted to 1.12 with water, the pH of the resulting solution was adjusted to pH 7.3 with hydrochloric acid, and the ammonium tungstate was crystallized by evaporation. The crystals were dried and heated at 500°C to convert the ammonium tungstate

to tungstic trioxide. The results of this test are shown in Tables II and III. This conventional procedure produced tungstic trioxide of high purity but with a mediocre extraction efficiency, as only 80 per cent of the tungsten was leached out of the scheelite concentrate. With this method, the consumption of chemical reagents was 0.7 g HCl and 0.5 g NH₃ per gram of tungsten treated.

A series of tests were then carried out to determine if a sodium tungstate solution, suitable as feed to a cation-exchanger, could be produced by direct decomposition of the scheelite concentrate with sodium hydroxide. In these tests, the leaching was done in open Teflon beakers at a temperature of 100°C for a period of 8 hours. The amount of sodium hydroxide used ranged from 1.4 to 4.4 g NaOH/g W. The results given in Table IV show that even when 10 gram-equivalents of sodium hydroxide per gram-equivalent of tungsten was used at a concentration of 770 g NaOH/l (Test 5), the tungsten extraction was only 86.3 per cent.

It is apparent that the low tungsten extraction coupled with high caustic requirements make this approach unattractive.

As the direct decomposition of the scheelite with sodium hydroxide was considered to be unsatisfactory, tests were done with the object of producing a sodium tungstate solution for ion-exchange treatment by first decomposing the concentrate with hydrochloric acid to produce tungstic acid and then dissolving the tungstic acid in sodium hydroxide solution. The conditions required for the decomposition of scheelite with hydrochloric acid were investigated in a series of nine tests. In this series, the concentrate was leached with 37 per cent HCl, using HCl/W weight ratios in the range of 0.7 to 4.0 g HCl/g W at temperatures ranging from 60-100°C for leach periods of from 1 to 3 hours.

The results of the tests investigating the hydrochloric acid decomposition are given in Table V. In the reaction, because the scheelite is converted to insoluble tungstic acid and soluble calcium chlo-

Table IV—Leaching the Scheelite Concentrate with Sodium Hydroxide

Test No.	Sodium Hydroxide		Tungsten Extraction %
	(g NaOH/g W)	(g/l)	
1.....	1.4	200	19.2
2.....	1.8	250	25.7
3.....	2.7	375	59.4
4.....	3.5	615	82.6
5.....	4.4	770	86.3

ride, and because more than 90 per cent of the CaO in the concentrate is present as scheelite, the efficiency of the decomposition step was based on the amount of calcium reporting in the leach liquor. Satisfactory results were obtained when the concentrate was leached with 1.3 HCl/g W at 100°C for 3 hours (Table V, Test 3). These conditions resulted in over 90 per cent of the scheelite being decomposed. A study of the results of Tests 5 to 9 (Table V) shows that the decomposition efficiency increases with temperature but that leaching for periods of more than 1 hour is not advantageous. The weight loss in these tests was approximately 10 per cent, and chemical analyses of the

leach liquor and residue showed that over 99.9 per cent of the tungsten remained in the solid residue, mainly as tungstic acid.

The residue containing the tungstic acid made by decomposing the scheelite concentrate with 0.7 g HCl/g W at 100°C for 3 hours (Table V, Test 5) was leached with sodium hydroxide to investigate the conditions required for this operation. In these tests, the filtered and washed solids from the hydrochloric acid decomposition step were slurried with water (about 3 parts of water to 1 part of solids by weight). The slurry was heated to either 70 or 100°C and the sodium hydroxide, in the form of a 20 per cent aqueous solution, was added to a pH of 8.0.

It required about 0.5 hour for the pH to reach 8.0, although leaching was continued for periods of 1, 3 or 5 hours, during which time only a small amount of sodium hydroxide was required to maintain the pH. The results shown in Table VI show that better than 96 per cent of the tungsten present in the scheelite concentrate was recovered as soluble sodium tungstate after leaching for 1 hour at 100°C (Test 1). The sodium hydroxide requirement for this step was about 0.4 g NaOH/g W.

The results obtained from the work on the hydrochloric acid decomposition of the scheelite concentrate, and the sodium hydroxide treatment of the tungstic acid, showed that this procedure provided an economical and easily controlled method for producing a suitable ion-exchange feed solution. Consequently, solution for the ion exchange study was prepared by decomposing the scheelite concentrate with hydrochloric acid under the conditions given in Table V, Test 3, and then leaching the solids from decomposition with sodium hydroxide under the conditions given in Table VI, Test 3. The solution obtained after filtering the slurry on completion of the sodium hydroxide leach contained more than 95 per cent of the tungsten present in the original scheelite concentrate at a concentration of 135 g W/l. The sodium to tungsten ratio in this solution was found to be equal to 0.93 g-eq W/g-eqNa.

The distribution of the elements present in the scheelite concentrate in the various products of the decomposition and dissolution steps described above are given in Table VII. These results show that the leaching operations used in the preparation of the ion-exchange feed solution were effective in eliminating a large proportion of the impurities through their elimination to waste in the filtrate from the hydrochloric acid decomposition filtrate and in the residue from the sodium hydroxide leach.

The sodium tungstate solution, containing about 135 gW/l, from the sodium hydroxide leach was divided into four equal parts and diluted with water to produce ion-exchange feed solutions containing tungsten concentrations ranging from 6.2 to 54.0 g W/l and, respectively, 1.8 to 14.5 gNa/l. The solutions were then passed through a column containing 200 ml of wet and settled Dowex 50Wx8 resin at a flow rate of 3 ml/min. In one test, the resin was regenerated

Table V—Leaching Scheelite Concentrate with Hydrochloric Acid

Test No.	37% HCl	Leach Conditions		Calcium Extraction (%)
	g HCl/g W	(Temp. °C)	(Time, hrs)	
1.....	4.0	100	3	89.4
2.....	2.6	100	3	92.6
3.....	1.3	100	3	92.3
4.....	0.9	100	3	91.3
5.....	0.7	100	3	88.6
6.....	0.7	100	2	84.6
7.....	0.7	100	1	87.0
8.....	0.7	80	3	72.1
9.....	0.7	60	3	69.0

Table VI—Leaching Crude Tungstic Acid with Sodium Hydroxide

Test No.	Sodium Hydroxide		Leach Conditions			Tungsten Extraction (%)
	(g NaOH/g W)	(g NaOH/l)	(Temp. °C)	(Time, hrs.)	pH	
1.....	0.41	62	100	1	8	96.5
2.....	0.41	62	100	3	8	96.5
3.....	0.41	62	100	5	8	96.5
4.....	0.43	64	70	1	8	95.4
5.....	0.43	64	70	3	8	95.4
6.....	0.43	64	70	5	8	95.7

Table VII—Distribution of Metallic Elements in Leach Products (per cent)

Element	Filtrate from NaOH Leach (ion-exchange feed)	Residue from NaOH Leach (to waste)	Filtrate from HCl Decomposition (to waste)
W.....	95.1	4.9	< 0.01
Na.....	99 +	< 1	0
CaO.....	0	11	89
Mn.....	1	86	13
Mg.....	4	44	52
Fe.....	3	80	17
Al.....	4	66	30
Cu.....	55	12	33
Ag.....	0	0	100
Si.....	5	95	0
V.....	37	63	0
Mo.....	90	10	0
Ti.....	44	56	0
Zr.....	0	100	0
Ni.....	0	100	0

Table VIII—Loading Tests with Dowex 50Wx8

Test No.	Resin Form	Feed Solution		Cumulative to Sodium Breakthrough					
		gW/l	gNa/g W	Effluent Solution		Resin Loading — per cent			
				ml	gNa/g W	Na	H	NH ₄	W
1.....	H	6.2	0.25	4000	0.0009	80	20	—	0
2.....	NH ₄	13.5	0.25	2000	0.0016	77	—	23	0
3.....	NH ₄	26.9	0.25	1000	0.0012	77	—	23	0
4.....	NH ₄	54.0	0.25	500	0.0005	77	—	23	0

Table IX—Regeneration Tests with Dowex 50Wx8

Test No.	Regenerating Solutions	Sodium Desorption		Regenerant Consumption	
		90% complete (ml)	99.9% complete (ml)	gNH ₄ Cl/g W	gHCl/g W
1.....	10% HCl	500	800	—	2.25
2.....	10% NH ₄ Cl	400	600	1.73	—
3.....	"	400	600	1.73	—
4.....	"	400	600	1.73	—

with 10 per cent hydrochloric acid; in three other tests, 10 per cent ammonium chloride was used as the regenerant. The results of these ion-exchange tests are shown in Tables VIII and IX.

Dowex 50Wx8 was effective in converting the sodium tungstate to either ammonium tungstate or tungstic acid, both of which may be converted conveniently to tungstic trioxide. The tungsten-bearing column effluents contained little sodium, about one part per thousand parts of tungsten, to the point where breakthrough of sodium occurred; it is foreseen that the sodium entrapment may be further decreased to a negligible quantity by close control of the breakthrough point. The results do indicate, however, that the tungsten was not adsorbed by the resin and that the primary action of the resin in adsorbing the sodium was efficient. These tests were carried to the full saturation of the resin with sodium and confirmed the specified capacity of Dowex 50Wx8; i.e., 1.9 g-eg/l of wet resin. The breakthrough of sodium was estimated to have occurred when 77 per cent of the resin sites had been exchanged with sodium. The consumptions of the regenerants were reasonable at 1.73 g NH₄Cl/g W and 2.25 g HCl/g W, considering that the resin is not much more selective for ammonium than for sodium and is less selective for hydrogen than for sodium (3).

The tungsten-bearing effluents were evaporated in Teflon beakers to crystallize the ammonium tungstate and tungstic acid. The crys-

Table X—Analysis of Tungstic Anhydride

Elements	Tungstic Anhydride		
	Commercial Product	Ion-Exchange Method NH ₄ Cl Regeneration Test 2, Table VI	Ion-Exchange Method HCl Regeneration Test 1, Table VI
W.....	77.4%	77.2%	77.4%
Al.....	< 1 ppm	< 1 ppm	< 1 ppm
As.....	< 0.005%	< 0.005%	< 0.005%
Bi.....	< 0.005%	< 0.005%	—
CaO.....	< 0.02%	< 0.02%	< 0.02%
Cu.....	< 0.1 ppm	4 ppm	0.4 ppm
Fe.....	< 0.01%	< 0.005%	0.004%
Mg.....	< 0.1 ppm	< 0.1 ppm	< 0.1 ppm
Mn.....	< 0.1 ppm	< 0.1 ppm	< 0.1 ppm
Na.....	7 ppm	< 5 ppm	ND
P.....	0.02%	< 0.01%	< 0.006%
S.....	< 0.01%	< 0.01%	< 0.01%
Si.....	33 ppm	11 ppm	53 ppm

tals were washed with 70 per cent nitric acid and water and ignited at about 600°C in platinum crucibles. The products of the ignition were identified as tungstic trioxide by X-ray diffraction method and analysed by precise chemical and spectrographic methods. The results of these analyses are reported in Table X. For the purposes of comparison, the analysis of a tungstic trioxide known to be suitable for the production of high-purity tungsten metal is also shown in Table X.

It is seen in Table X that the tungstic trioxide produced by the ion-exchange methods contained few impurities and is certainly equivalent in chemical purity to that available commercially for the production of high-purity tungsten metal. The difference between the silicon contents of the tungstic trioxide produced by the two methods with the ion-exchanger is

significant, as about five times as much was contained in the product from the HCl regeneration; the authors have no explanation for this, except that the silicon may have been due to contamination of the products through handling in glassware.

Discussion

The investigation has established that hydrochloric acid effectively attacks the scheelite concentrate tested to produce crude tungstic acid. The tungstic acid may be dissolved in either ammonium hydroxide or sodium hydroxide. The results given in Table II show that with ammonium hydroxide only 80 per cent of the tungsten is recovered from the concentrate, even when an appreciable excess of ammonia is used, while the results given in Table VI show that with sodium hydroxide, in slight excess, 96 per cent of the tungsten is re-

Table XI—Reagent Consumption and Costs

	Consumption lb/lb W Treated	W Recovery per cent	Consumption lb/lb W Recovered	Unit Cost* 100% basis	Cost per lb W Recovered
<i>Ammonia Method</i>		80			
Hydrochloric Acid.....	0.7		0.9	\$0.047	\$0.042
Ammonia.....	0.5		0.6	0.047	0.028
WO ₃ (71.3% WO ₃ contained in scheelite concentrate) at \$ 20/short ton unit of WO ₃	1.26		1.575	1.00	1.575
Total.....					\$1.645
<i>Ion-exchange Method NH₄Cl Elution</i>		96			
Hydrochloric Acid.....	0.7		0.7	\$0.047	\$0.033
Sodium Hydroxide.....	0.4		0.4	0.058	0.023
Ammonium Chloride.....	1.73		1.80	0.060	0.108
WO ₃ (71.3% WO ₃ contained in scheelite concentrate) at \$ 20/short ton unit of WO ₃	1.26		1.312	1.00	1.312
Total.....					\$1.476
<i>Ion-exchange Method HCl Elution</i>		96			
Hydrochloric Acid.....	2.95		3.073	\$0.047	\$0.144
Sodium Hydroxide.....	0.4		0.4	0.058	0.023
WO ₃ (71.3% WO ₃ contained in scheelite concentrate) at \$ 20/short ton unit of WO ₃	1.26		1.312	1.00	1.312
Total.....					\$1.479

*Chemical costs were based on market prices published in *Oil, Paint and Drug Reporter*, 100 Church St., N. Y., December 6, 1965. The price of the scheelite concentrate is based on current market value.

covered from the concentrate.

When ammonium hydroxide was used to dissolve the tungstic acid, producing ammonium tungstate, the final tungstic trioxide was obtained by recrystallizing the ammonium tungstate once to eliminate impurities, and then converting the ammonium tungstate to tungstic trioxide by thermal decomposition. When sodium hydroxide was used to dissolve the tungstic acid, producing sodium tungstate, the final tungstic trioxide was obtained by converting the sodium tungstate either to ammonium tungstate or to tungstic acid by passing the sodium tungstate solution through Dowex 50Wx8 ion-exchange resin, recovering the ammonium tungstate or tungstic acid by crystallization, and finally converting to tungstic trioxide by thermal decomposition. The purity of the tungstic trioxide obtained by all the methods tested was similar and chemically equivalent to a commercial product suitable for producing tungsten metal of high purity.

The Dowex 50Wx8 resin was shown to be effective in its primary function of converting the sodium tungstate solution to either ammonium tungstate or tungstic acid, compounds of tungsten that are readily convertible to tungstic trioxide. The sodium hydroxide leach solutions contained only small

quantities of cation impurities, and the secondary role of the resin in adsorbing them from the solution was not clearly established. The sodium hydroxide - Dowex 50Wx8 method is advantageous in that only 0.41 gNaOH/g W is required to leach 96 per cent of the tungsten, whereas 0.5 gNH₃/g W is required by the ammonia leach to extract only 80 per cent of the tungsten in the concentrate. Table XI shows that the higher recovery obtained using sodium hydroxide more than compensates for the higher reagent costs involved in the ion exchange operation; i.e., 1.73 g NH₄Cl/g W or 2.25 g HCl/g W.

The attempt to leach scheelite concentrate with sodium hydroxide to produce sodium tungstate directly was not encouraging, as only 86 per cent of the tungsten was extracted from the concentrate and the consumption of sodium hydroxide was high.

Conclusions

An improved process for preparing tungstic trioxide from scheelite concentrate has been developed. It consists of decomposing the scheelite in hydrochloric acid to produce tungstic acid; the latter is then dissolved with sodium hydroxide to form sodium tungstate in solution. The sodium tungstate solution is converted to am-

monium tungstate by ion-exchange using Dowex 50Wx8, and the ammonium tungstate is finally thermally decomposed to tungstic trioxide. The recovery of tungsten is 96 per cent compared with 80 per cent for the conventional process, and the tungstic trioxide produced is of satisfactory purity.

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