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*IMPROVEMENT OF A CONTINUOUS PROCESS
FOR THE PRODUCTION OF HIGH-PURITY
TUNGSTIC TRIOXIDE FROM SCHEELITE:
PRELEACHING THE SCHEELITE WITH
WEAK HYDROCHLORIC ACID*

J. A. VEZINA AND W. A. GOW
EXTRACTION METALLURGY DIVISION
DECEMBER 1969

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IMPROVEMENT OF A CONTINUOUS PROCESS FOR THE PRODUCTION
OF HIGH-PURITY TUNGSTIC TRIOXIDE FROM SCHEELITE:
PRELEACHING THE SCHEELITE WITH WEAK HYDROCHLORIC ACID

by

J. A. Vezina* and W. A. Gow**

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ABSTRACT

The effect of leaching Canadian scheelite concentrates with weak hydrochloric acid at pH 1.0 prior to treatment by a previously described Mines Branch process was investigated. The work showed that the weak-acid leach removed about 25 per cent of the iron, 90 per cent of the phosphorus, 10 per cent of the calcium and 0.1 per cent of the tungsten from a scheelite concentrate analysing 54.4 per cent WO_3 , 15.8 per cent CaO, 3.9 per cent Fe, and 0.43 per cent P. The overall cost on the basis of acid consumption and tungsten loss would be about \$0.04 less per pound of tungsten than for the original Mines Branch process where the weak-acid leach was not used.

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Direction des mines

Bulletin technique TB 104

AMÉLIORATION D'UN PROCÉDÉ CONTINU DE PRODUCTION DE
TRIOXIDE TUNGSTIQUE DE GRANDE PURETÉ À PARTIR DE
LA SCHEELITE: PRÉLESSIVAGE DE LA SCHEELITE À
L'ACIDE CHLORHYDRIQUE

par

J. A. Vézina et W. A. Gow

RÉSUMÉ

Les auteurs ont poursuivi des recherches sur l'effet de lessiver des concentrés de scheelite canadienne dans une solution de pH 1,0 en se servant d'acide chlorhydrique faible, avant de les traiter selon une méthode d'extraction de la Direction des mines, décrite précédemment. Les résultats ont démontré que le lessivage à l'acide faible libérait environ 25 p. 100 du fer, 90 p. 100 du phosphore, 10 p. 100 du calcium et 0.1 p. 100 du tungstène d'un concentré de scheelite composé de 54.4 p. 100 de WO_3 , 15.8 p. 100 de CaO, 3.9 p. 100 de Fe et 0.43 p. 100 de phosphore. Le coût global, fondé sur la consommation d'acide et la perte de tungstène, serait d'environ 4 cents de moins la livre de tungstène comparativement au coût du procédé original de la Direction des mines, lequel ne comprenait pas l'emploi du lessivage à l'acide faible.

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CONTENTS

	<u>Page</u>
Abstract	i
Résumé	ii
Introduction	1
Procedure	1
Experimental Results	2
Discussion	5
Conclusions	7
References	7
Acknowledgements	7

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TABLES

<u>No.</u>		<u>Page</u>
1.	Analysis of Scheelite Concentrate, Per cent	2
2.	Use of the Acid in Preleaching a Scheelite Concentrate	3
3.	Extraction in Preleach Solution, Per Cent	3
4.	Decomposition of Scheelite Concentrate with Concentrated HCl after being Leached with Weak HCl at pH 1.0	4
5.	Dissolution of Crude Tungstic Acid (Table 4) with Sodium Hydroxide	4
6.	Decomposition of Scheelite Concentrate Directly with Concentrated Hydrochloric Acid	5
7.	Decomposition of Crude Tungstic Acid (Table 6) with Sodium Hydroxide	5
8.	Economic Advantage of Preleaching Based on Reagent Consumption and Tungsten Recovery	6

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INTRODUCTION

In a paper presented in 1967 by the authors (1), a general procedure for processing low-grade Canadian scheelite concentrates for the production of tungstic trioxide and ammonium paratungstate was described. That procedure consisted of decomposing the scheelite mineral with hydrochloric acid, dissolving the resulting crude tungstic acid with sodium hydroxide, and then converting the sodium tungstate to ammonium tungstate by means of a cation exchange resin. With this process, some of the acid-soluble impurities present in the scheelite concentrate, such as iron, calcium and phosphorus, report in the sodium tungstate solution and finally, to a large extent, in the tungsten product. The work described in the present report was done to ascertain whether a weak hydrochloric acid leach done ahead of the scheelite decomposition step mentioned above would preferentially leach out the undesirable impurities.

It has been common practice to upgrade scheelite gravity and flotation concentrates by a weak hydrochloric acid leach. Previous work, unpublished, done at the Mines Branch has shown that maximum dissolution of impurities with minimum dissolution of tungsten is effected at a pH of not less than 1.0 at a temperature of not greater than 60°C.

The results of the work described in this bulletin provide a comparison of the impurity levels of sodium tungstate solutions produced directly from a relatively low-grade scheelite concentrate and from the same concentrate after it had been leached with weak hydrochloric acid.

PROCEDURE

The scheelite concentrate used in this investigation was supplied through the courtesy of the Canada Tungsten Mining Corporation Limited, and was an intermediate-grade concentrate produced in the company's concentration plant. The analysis of the concentrate is reported in Table 1.

TABLE I

Analysis of Scheelite Concentrate, Per Cent

<u>By Analytical Methods</u>		<u>By Spectrographic Method</u>	
WO ₃	56.4	Al	0.29
CaO	15.8	Mn	0.19
SiO ₂	8.21	Mg	0.41
Mo	0.009	-	-
Fe	3.91	Ti	0.07
P	0.43	Cu	0.03
S	0.13		
As	<0.01		
Bi	0.12		
K	0.32		

The tests were carried out with standard laboratory equipment. An 800g batch of the concentrate was contacted with a dilute solution of hydrochloric acid in a 3-litre, electrically heated glass kettle for three hours while maintaining the temperature and pH of the leach solution constant at 60°C and pH 1.0 respectively. The leach solution was then filtered, using a Büchner funnel. The solids were washed thoroughly with distilled water. The upgraded scheelite concentrate was divided into four equal parts. Each portion was contacted with a different quantity of hydrochloric acid in a 2-litre glass kettle for three hours under vigorous agitation while the temperature was controlled at 100°C. A water-cooled reflux condenser was used in conjunction with the kettle, to prevent acid losses.

The slurry was filtered and the crude tungstic acid was washed thoroughly with distilled water. The washed tungstic acid was then leached, using a solution of sodium hydroxide of concentration 60.7 grams NaOH per litre to control the pH of the leach solution at pH 8.0. This leach was carried out at 90°C for a duration of 5 hours.

EXPERIMENTAL RESULTS

Leaching the scheelite concentrate with dilute hydrochloric acid at pH 1.0 and 60°C for 3 hours required 0.104 gram of hydrochloric acid per gram of tungsten in the

concentrate. Table 2 shows that 75.4 per cent of this acid was consumed, mainly to dissolve calcium- and iron-bearing minerals. In the preleach operation, the concentrate lost 6.25 per cent of its weight and, as shown in Table 3, most of the tungsten was recovered in the upgraded concentrate which contained the equivalent of 59.9 per cent WO_3 .

TABLE 2

Use of the Acid in Preleaching a Scheelite Concentrate

Combined with iron	28.43 per cent
Combined with calcium	43.75 per cent
Combined with other elements	3.22 per cent
Residual acid	25.30 per cent

Table 3 shows that the weak-acid leach was effective in dissolving an appreciable quantity of phosphorus, but was not as effective in dissolving iron and calcium. Only 36.4 per cent of the calcium that was not combined as $CaWO_3$ was dissolved.

TABLE 3

Extraction in Preleach Solution, Per Cent

W	Ca	Fe	P
0.093	8.73	22.19	89.20

The upgraded concentrate from the weak-acid leach was next divided into four equal parts and then decomposed with various amounts of concentrated hydrochloric acid, at a temperature of $100^{\circ}C$ for a duration of 3 hours, to produce crude tungstic acid. Four tests were done, in which the quantity of hydrochloric acid used ranged from 0.51 to 1.20 grams of hydrochloric acid per gram of tungsten contained in the concentrate. The crude tungstic acid produced was washed with water and then decomposed in a solution of sodium hydroxide. The caustic leach was done at a pH of 8.0 and a temperature of $90^{\circ}C$, for a duration of 5 hours. The results of these four tests are shown in Tables 4 and 5.

TABLE 4

Decomposition of Scheelite Concentrate with Concentrated
HCl after being Leached with Weak HCl at pH 1.0

Test No.	Acid Used, g HCl/g W	Per Cent of Acid Consumed	Cumulative Extraction*, per cent			
			W	Ca	Fe	P
1	0.51	98.50	0.16	75.68	68.80	89.20
2	0.72	88.30	0.11	93.49	75.67	89.20
3	0.86	78.10	0.09	95.20	81.97	89.20
4	1.20	64.86	0.11	95.70	84.78	89.20

*Includes preleach extraction.

TABLE 5

Dissolution of Crude Tungstic Acid (Table 4)
with Sodium Hydroxide

Test No.	Sodium Hydroxide Used, g NaOH/g W	Tungsten Extraction, per cent	Overall Tungsten Recovery, per cent	Analyses of Sodium Tungstate Solutions, Parts per 100 Parts of Tungsten		
				Ca	Fe	P
1	0.376	73.33	73.22	0.002	0.417	0.076
2	0.468	96.02	95.91	0.002	0.254	0.065
3	0.483	99.39	99.30	0.054	0.161	0.032
4	0.467	99.69	99.58	0.109	0.285	0.076

To evaluate the effectiveness of the weak-acid leach, four batches of concentrate were treated as above but without using the weak-acid leach. In these tests the scheelite concentrate was decomposed with amounts of hydrochloric acid ranging from 0.51 to 1.45 g HCl per g W in the concentrate. The four lots of crude tungstic acid so produced were then dissolved in a solution of sodium hydroxide to produce sodium tungstate. The results of these tests are shown in Tables 6 and 7.

A comparison of the results given in Tables 5 and 7 shows that, where the weak-acid leach was used (Table 5), higher recoveries of tungsten and lower impurity levels in the final sodium tungstate solution were obtained.

TABLE 6

Decomposition of Scheelite Concentrate Directly
with Concentrated Hydrochloric Acid

Test No.	Acid Used, g HCl/g W	Per Cent of Acid Consumed	Extraction, per cent			
			W	Ca	Fe	P
5	0.57	98.84	0.04	67.45	61.00	9.13
6	0.82	95.12	0.04	91.67	62.49	13.13
7	1.08	83.55	0.05	95.26	78.64	18.22
8	1.45	66.15	0.05	95.18	85.07	23.66

TABLE 7

Decomposition of Crude Tungstic Acid (Table 6)
with Sodium Hydroxide

Test No.	Sodium Hydroxide Used, g NaOH/g W	Tungsten Extraction, per cent	Overall Tungsten Recovery, per cent	Analyses of Sodium Tungstate Solutions, Parts per 100 Parts of Tungsten		
				Ca	Fe	P
5	0.367	67.94	67.93	0.107	0.698	0.954
6	0.500	88.43	88.40	0.098	0.721	0.914
7	0.540	98.30	98.26	0.243	0.547	1.094
8	0.523	98.51	98.46	0.128	0.506	0.982

DISCUSSION

Although the weak-hydrochloric-acid leach of the raw scheelite concentrate reduced the impurity level in the sodium tungstate solution subsequently produced, it is not known from this study whether or not the procedure would reduce the impurity levels of low-grade concentrates to the point where

no further treatment for impurity removal would be needed. If further treatment were necessary--precipitation with magnesium and ammonium chlorides, for example⁽²⁾--there would be no advantage in doing the weak-acid leach as well. This point would have to be studied further by any scheelite producer contemplating the chemical refining, by the Mines Branch process ⁽¹⁾, of specific scheelite concentrates.

Table 8 shows that, on the basis of reagent cost and tungsten recovery only, the use of a weak-acid leach would reduce the overall cost of the process up to the production of sodium tungstate solution by \$0.038 per pound of tungsten (Tests 3 and 7). This figure does not take into account the cost of the heat used in the weak acid-leach, nor the additional capital charges involved, which could well nullify the acid-cost advantage realized when preleaching was done.

TABLE 8

Economic Advantage of Preleaching Based on Reagent
Consumption and Tungsten Recovery

Test No.	Weak Acid Leach HCl**		Decomposition HCl*		Sodium Hydroxide**		Tungsten Losses***		Total
	lb/lb W	\$/lb W	lb/lb W	\$/lb W	lb/lb W	\$/lb W	lb/lb W	\$/lb W	
1	0.104	0.006	0.51	0.029	0.376	0.029	0.268	0.742	0.806
2	0.104	0.006	0.72	0.041	0.468	0.037	0.041	0.113	0.197
3	0.104	0.006	0.86	0.049	0.483	0.038	0.007	0.019	0.112
4	0.104	0.006	1.20	0.068	0.467	0.037	0.004	0.011	0.122
5	-		0.57	0.032	0.367	0.029	0.321	0.889	0.950
6	-		0.82	0.047	0.500	0.039	0.116	0.322	0.408
7	-		1.08	0.061	0.540	0.042	0.017	0.047	0.150
8	-		1.45	0.082	0.523	0.042	0.015	0.041	0.165

* Basis 100% HCl, unit cost \$0.0568/lb. ⁽³⁾

** Basis 100% NaOH, unit cost \$0.0783/lb. ⁽³⁾

*** Basis \$2.77 per pound of tungsten. ⁽²⁾

CONCLUSIONS

Weak-hydrochloric-acid leaching, at 60°C and pH 1.0, of a scheelite concentrate of intermediate grade produced by Canada Tungsten Mining Corporation Limited will decrease the iron content of the concentrate by about 25 per cent, the phosphorus content by about 90 per cent, and the calcium content by about 10 per cent. The weak-acid leach has the additional advantage of decreasing the cost of the acid used in the Mines Branch process, but the cost of the heat and the capital expenditure entailed in the preleaching may possibly absorb this economic advantage.

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