THE MANUFACTURE
of
TUNGSTIC ACID
from
SCHEELITE

Thesis

by

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INTRODUCTION.

The chief source of tungsten at the present time is wolframite which is a tungstate of manganese and iron. It is found in numerous portions of the earth's surface and the various deposits have been more or less completely exploited. In recent years deposits of scheelite, a tungstate of calcium, have been discovered in several countries. In the United States the largest deposits are found in California and Arizona, but these have not yet been worked to any extent.

Whatever the ore, the first step in the manufacture of tungsten, after the concentration of the raw ore, is the formation of tungstic acid. The metal is then obtained by dehydration and reduction of the acid. Whereas the complete reduction of the acid with carbon is a comparativly simple process, the preparation of the acid from the ores presents numerous difficulties which have to be overcome before any method can be used commercially. The methods now being used are of three general types,- decomposition of the ore by acid treatment, by interaction with caustic alkali, or by fusion with soda ash. The descriptions of these methods which are found in the literature, are of a general nature, as the processes are all patented. They deal almost wholly with wolframite.

, The object of this research was to develop an industrial method for the preparation of Tungstic acid from Scheelite.

EXPERIMENTAL PART

The scheelite used in this investigation was a sample of concentrates from Arizona. Analysis gave the following results:

Loss on Ignition	0.33	per	cent
Insoluble residue	19.28	"	"
Tungstic Oxide (WO_3)	55.10	"	"
Iron (Fe_2O_3) Alumina (Al_2O_3)	2.85	"	"
Calcium (CaO)	20.12	"	"
Magnesium (Mgo)	Trace		
	97,70		

The sample for analysis was decomposed by repeated evaporation with hydrochloric acid and nitric acids. The undetermined constituents and experimental error amounted to 2.3%. A content of 55.10% tungstic acid (WO_3) corresponds to 43.7% tungsten (W), 59.4% tungstic acid (H_2WO_4) and 68.5% calcium tungstate ($CaWO_4$). Pure Scheelite contains 80.6% tungstic Oxide (WO_3) and 19.4% lime (CaO)

A number of preliminary tests were first made to determine which of the three general methods was best for decomposing the scheelite. Concentrated hydrochloric acid attacked the ore only after long boiling. The precipitate of tungstic acid seemed to have an apparent specific gravity, less than that of the undecomposed material, but complete separation of the two was difficult.

Boiling with caustic solutions as strong as 50% NaOH under atmospheric pressure, did not decompose the sample to any appreciable extent.

Fusion of the scheelite with soda ash seemed to be the most promising, and hence it was decided to confine experimentation to the development of this method.

The procedure consisted of fusing the intimately mixed ore and flux material contained in a fireclay crucible in a small gas-fired furnace. The melt was lixiviated with water, the insoluble residue filtered off, the clear filtrate concentrated somewhat by evaporation, and the tungstic acid precipitated by pouring the hot solution into boiling hydrochloric acid. The acid was filtered off, washed with hot dilute acid (washing with water alone converts some of the acid into the colloidal form which goes through the filter) and the tungstic acid dried to constant weight at 110°C.

It was found that best yields could be obtained when the molten mix was poured directly into water. This could, however, be successfully done only within a narrow range of conditions. The precipitation of the tungstic acid was not complete, but that remaining in solution could be recovered by neutralizing the acid filtrate with caustic soda, filtering off the precipitate of iron and alumina, and precipitating a second time by pouring into hot hydrochloric acid.

Complete decomposition of the scheelite by fusion was not obtained. The residue remaining after lixiviation always contained tungsten, about one third of which could be recovered as tungstic acid by treatment with hydrochloric acid, dissolving out the precipitated tungstic acid with ammonia and reprecipitating with hydrochloric acid.

In none of the reactions where hydrochloric acid was used could sulfuric acid be satisfactorily substituted.

The average yield from the more successful runs was 50% tungstic acid and as the scheelite contained 59.4%, the recovery was thus about 85%. The actual data on proportions of mix, time of fusion, etc., are given in the appended table at the end of the thesis.

OUTLINE OF THE PROCESS.

The following procedure is recommended:

1. Mix 100 parts of finely ground scheelite with 60 parts of soda ash, and fuse the mixture for an hour at about 800°C.

2. Pour the molten mass into water and heat to boiling with constant stirring.

3. Allow the insoluble residue to settle and pour off the clear solution.

4. Evaporate the solution from (3) until the concentration of the sodium tungstate is about 20%.

5. Pour the hot concentrated solution into 114 lbs. of hot muriatic acid and boil for 15 minutes.

6. Allow the precipitated tungstic acid to settle, pour off the acid liquor.

7. Wash with hot water containing a trace of muriatic acid, filter and dry.

8. Neutralize the acid liquor from (6) with solid caustic soda, boil and filter from any precipitate which may form.

9. Pour the filtrate into 50 lbs. muriatic acid and proceed as in (6) and (7).

10. Wash the insoluble residue from (3) with hot water. These washings are used for lixiviation in (2).

11. Decompose the residue by ~~testing~~ treating with 125 lbs. muriatic acid.

12. Allow the tungstic acid and residue to settle, pour off the liquid and wash.

13. Dissolve out the tungstic acid with 4.65 lbs. ammonia and filter from the insoluble material.

14. Pour the ammoniacal filtrate into 20 lbs. muriatic acid and proceed as in (6) and (7).

COST DATA.

The cost of the materials used and value of the tungstic acid obtained was calculated on the basis of 100 lbs. scheelite and on current quotations. The various quantities are itemized separately to show the amounts used in the successive steps in the process.

100 lbs.Scheelite @ 9.25 perunit	25.50			
60 lbs.Soda ash @ 1.25 per cwt......	0.75			
114 lbs.Muriatic acid @ 0.80 per cwt......	0.90		41 lbs.Tungstic Acid @ 1.25 per lb...	51.25
	27.15			
16 lbs.Caustic soda @ 3.50 per cwt...	0.55			
50 lbs.muriatic acid	0.40		3.5 lbs.Tungstic Acid	4.35
	0.95			
125 lbs. muriatic acid	1.00			
4.65 lbs.ammonia @ .06½ per lb.	0.30		44 lbs. Tungstic Acid	5.50
20 lbs.muriatic acid	0.15			
	1.45			$61.10
		29.45		
Value of product over and above cost of materials.....		31.65		
		61.10		

The balance shown above does not, of course, represent a net balance in favor of the process. To the cost of materials as shown above would have to be added the cost of fuel and labor for the various operations, the depreciation of the apparatus and the interest on the original investment. Since the scale on which the experiments have been so far carried out, does not warrant an estimate of these items, further investigation remains to be done before the manufacture of tungstic acid from scheelite could be undertaken on a commercial basis.

EXPERIMENTAL DATA.

No.	Scheelite (grams)	Flux (grams)	Time Heated	Yield H_2WO_4.	Observations
8	50	Na_2CO_3 -20	---	II %	Melt almost solid;long heating.
9	20	" -7.4	Till w. hot.	———	Pouring into water caused explosion with loss of materials
I0	20	" -I0	½ Hr.	29 %	Cooled melt finely ground and lixiviated with steam injection
II	20	" -7.4 NaOH -2	"	24.5 %	Same as in No. I0.
I2	20	Na_2CO_3 -I0 NaOH -2	"	4.9 %	Melt fused to the crucible. Treated as in No. I0.
I3	20	Na_2CO_3 -4 NaOH -3	"	40.2 %	Cooled melt very hard. Treated as in No. I0.
I4	20	$NaHCO_3$ -II.5	"	I6.2 %	" " " " "
I5	20	" -I5	"	25 %	" " " " "
I6	20	" - 6 Na_2CO_3 - 4	"	I5.5 %	" " " " "
I7	20	NaOH - 5.4	"	6.I %	" " " " "
I8	20	" - 8	"	6.0 %	" " " " "
I9	60	Na_2CO_3 HCl.	"	Cooled melt ground and lixiviated by boiling in water;sol.divided into 5 equal portions: a,25cc.poured into sol.9.5%;b.Sol.into 25cc.HCl.II%; c.As a. but Icc.HNO_3 added,9.5%;d.As b.butIcc.HNO_3 added,I0.8%;e.Sol.evaporated to half the volume,II.8%.	

No.	Scheelite (grams)	Flux (grams)	Time Heated	Yield H_2WO_4	Observations
20	60	Na_2CO_3-30	½Hour	a. I7% b. I9%	Cool melt ground.Two samples analyzed:a.Boiled in water for I½ Hours.b.2½ Hours.
24	I00	" -50	"	27%	Melt poured into water.
25	I00	" -50 NaOH -5	Fused &I Hr.	25%	" " " "
26	I00	" -I5 Na_2CO_3-20	Long	I2%	Would not melt after prolonged heating.
27	I00	" -50 NaOH-5;NaCl-I0.	IHour	43%	Melt just fluid enough for pouring into water.
28	I50	Na_2CO_3- 75	2Hours	a.4.7% b.22%	Could not not poured into water From top of cruc.b. From bottom
29	I00	" - 50	"	I7%	Just fluid enough for pouring.
30	I50	"-75;NaCl-30.	2/3Hrs.	I5%	Poured into water.
3I	I50	" -75; " -I5; NaOH-7.5	2 Hrs.	———	Pasty.Pouring into water caused explosion.Material lost.
32	Repeat on No.3I with same result.				
33	I50	Na_2CO_3-I00	I Hr.	26.6%	Poured into water.
34	I50	" "	2 Hrs.	28%	More difficult to pour.
35	I50	Soda Ash-I20	"	36%	Semi-fluid. Poured into water.
36	I00	" " -I00	"	20%	Very fluid.Pouring into water caused explosion.Poured intomould
37	I00	" " -75	I¾ Hrs.	I5%	Same as No. 36.
38	I50	" " -I20	a.2 " b.3 "	a.44% b.32%	Same as No.36.Portion poured out.b.Heated I Hr.more.
39	50	" " -40	2 Hrs.	6.4%	Heated at low temperature.
40	I00	" " -60	I Hr.	3I%&3%	Same as No.36.

No	Scheelite (grams)	Flux (grams)	Time Heated	Yield H_2WO_4	Observations.
41	I00	Soda Ash-70	I Hr.	26%;4%	Same as No.36.
42	I00	" " -80	I "	I8%;I.5%	" " " "
43	I50	" " -75	I "	I6.3%	Pasty. Treated as in No.36.
44	I00	" " -60	½ "	a. I2%;4% b. II%3%	Sol.inb.twice as concentrated as in a.
45	I00	" " -60	¾ "	II%;7%	Treated as in No. 36.
46	I00	" " -60	I "	I9.5%; 4.0%	" " " " "
47	I00	" " -60	I½ Hrs.	23.5%; 4.5%	" " " " "
48	I00	" " -60	I Hr.	24%; I6%.	Heated at about 800oC.Poured into water in a large vessel.
49	I00	" " -60 NaNO3 -I0	I Hr.	34%; 3%.	Treated as in No. 48.
50	I00	Soda Ash -69	I Hr.	39.5% 5.0% 4.4%	From first precipitation. " second " " acid recovery.
51	I00	" " -60	I Hr.	42.5% 2.0% 4.4%	" first precipitation. " second " " acid recovery.

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