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BROWN OXIDE BY-PRODUCT RECOVERY.
[PART] I.

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BROWN OXIDE BY-PRODUCT RECOVERY-I

Introduction

The increased difficulty of obtaining high-quality uranium concentrates has made it desirable to investigate the possibility of processing lower grade materials. The residues from the brown oxide purification process contain appreciable amounts of uranium. Also, there is available a carnotite concentrate from Western Colorado, which was to contain approximately 50% uranium oxide (U_3O_8) and 25% vanadium trioxide (V_2O_3). The recovery of vanadium from the carnotite sludge as a by-product would be necessary.

Object

To investigate the feasibility of obtaining uranium from the carnotite sludge in such a form as to permit its use in the brown oxide purification process.

Summary and Conclusions

Two possible methods for obtaining uranium from carnotite sludge have been outlined and their feasibility has been briefly investigated. The sludge which was available for experimental work contained, when dried, 46.9% uranium oxide (U_3O_8), 21.5% vanadium trioxide (V_2O_3), 10.7% sulfate, 7.84% sodium, and 4.1% chloride.

Method A.

This method was to consist of the following four steps:

1. Leach the sludge with hot water or caustic in an attempt to remove vanadium trioxide, sodium, chloride, and sulfate.
2. Dissolve the leached cake in nitric acid at a pH of 2.85 (1-100 dilution).
3. Filter, concentrate, and extract the resulting hex solution.
4. Recover vanadium from filtrate obtained in 1.

A hot water or caustic leach is effective in removing chloride and sulfate, but does not remove appreciable amounts of vanadium. A water leach reduces the sodium content of the cake to 0.16%, while a caustic leach leaves 2.5-5.0% sodium in the cake. In all cases the leached cake filters very slowly.

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When the leached cake is dissolved in nitric acid and the pH adjusted to 2.85 (1-100 dilution), a considerable amount of precipitate is obtained. This amounts to 50-80% by weight of the material used. The filtrate is free of vanadium as determined by a sodium peroxide test.

When the filtered hex is concentrated and extracted with ether, a very stable emulsion forms. This can not be broken by any of the methods known at present.

Method B.

This was to consist of the five following steps:

1. Heat the sludge to 700-800°C in the presence of carbon and sodium carbonate.
2. Leach the melt with hot water to separate soluble sodium salts from black oxide.
3. Dissolve the black oxide in nitric acid at a pH of 2.85 (1-100 dilution).
4. Filter, concentrate, and extract the resulting hex solution.
5. Recover the vanadium from filtrate obtained in 2.

When the sludge is heated to 700-800°C in the presence of 12% by weight of carbon and 32% by weight of sodium carbonate, the uranium is converted to black oxide and the vanadium is rendered soluble in water. Using the potassium ferrocyanide test for uranium and the sodium peroxide test for vanadium, it is found that the black oxide is free of vanadium and the solution from the water leach is free of uranium. Also the black oxide is sufficiently free of sodium, chloride, and sulfate. The black oxide obtained may be dissolved in nitric acid, filtered, and extracted in the usual way.

Experimental Details and Discussion

Method A.

A sample of the sludge was slurried with caustic solutions of various concentrations, stirred mechanically for one hour, filtered, and washed. Columns 1 and 2 of this table give the experiment number and weight of the sample used referred to a dry basis. The third column gives the amount and kind of solution employed and the time and temperature used in the leaching operation. Also are listed the amounts of water required to wash the leached cake. The filtrate was tested qualitatively and found to contain vanadium but not uranium. Columns 4 through 10 list the dry weight of the leached cake, the per cent loss in weight on leaching, and give the uranium, vanadium, sodium, sulfate, and chloride analysis.

Leached cake was dissolved in boiling nitric acid and the pH adjusted to 2.85 on 1-100 dilution scale. In making the final adjustment on the pH, sodium salts were used in experiments 2 and 3, and black oxide in experiments 5 and 7. The amounts of material involved are listed in column 1 in Table IB. Column 2 gives the weight of the material which is insoluble in nitric acid at the above pH. This insoluble material was not washed, but it was dried before weighing. Column 3 gives the calculated per cent of the total material which is insoluble in nitric acid. The filtrates obtained were found to be free of vanadium as determined by the sodium peroxide test. When boiled down to hex and extracted in the usual way, very stable emulsions formed.

Discussion of Results

Method A.

In the unleached material, the weight ratio of vanadium trioxide to uranium oxide is roughly 0.45. A water leach at 100°C and a 2% caustic leach at 80°C for one hour are not effective in reducing this ratio. At 100°C, 2% and stronger caustic solutions appear to remove up to one-third of the vanadium. The possibility exists that continued boiling with caustic for longer times will be more effective.

In all the experiments, chloride and sulfate were satisfactorily removed. The sodium content of the leached cake varied between 0.16% and 5%. The latter value in itself is not exceedingly high. The fact that the water leach removed practically all the sodium and sulfate indicates that the uranium and vanadium are chemically combined. At least, previous experiments with sodium salts have shown that such a treatment will not remove notable amounts of either sodium or sulfate.

When the leached cake is dissolved in boiling nitric acid and the pH adjusted to 2.85 on the 1-100 dilution scale, considerable insoluble material forms. The filtrate is vanadium-free according to the peroxide test. The chemical composition of the insoluble material is not known. If one assumes it to be uranyl vanadate, the per cent of the cake which does not dissolve may be calculated. In runs 3, 2, and 7, the calculated "insolubilities" are in reasonable agreement with the measured ones. The per cent insoluble material obtained in runs 5 and 6 is unaccountably high.

The filtrates obtained by dissolving the leached cake were used to carry out an extraction test. In each case very stable emulsions were formed. The usual methods for breaking these emulsions (recirculation, removal of water layer, or addition of more ether) were of no avail. The emulsion, however, did break up after standing 24 hours or more.

Experimental Details and Discussion

Method B.

50 grams of the dried sludge were mixed with six grams of carbon and 16 grams of anhydrous sodium carbonate. The mixture was placed in a

nickel dish and heated in the electric furnace. The product material was then leached with hot water, filtered and washed. The variations in the treatment and the results obtained are given in Table II.

Columns one and two list the experiment number and dry weight of sludge used. The time and temperatures employed in the heating operation are listed in column three together with the volume of filtrate obtained in leaching the melt. The weight of the dried leached cake and the amount of vanadium trioxide obtained in the filtrate are listed in columns four and five. According to the analysis of the original material, 23 grams of black oxide should be present in the leached cake, and 10.7 grams of vanadium pentoxide in the filtrate.

The results of qualitative tests for uranium and vanadium in the leached cake and filtrate are given in columns six and seven. It is apparent that a relatively clear separation of these elements can be obtained at temperatures above 650°C. The results of the chemical analysis carried out on the leached cake are given in columns 8 through 14. A small scale extraction test was carried out on the residues from experiments 8, 10, 11, and 12. A clean separation of the immiscible layers was obtained.

Table IA

Leaching Of Vanadium Sludge

Expt.	Dry Wt. Sample (grams)	Leaching Conditions	Wt. dry leached cake (grams)	Loss in wt. on leaching	Composition (per cent)				
					U ₃ O ₈	V ₂ O ₅	Na	SO ₄	Cl
1	454	1/2 gal. of water 1 hr. at boiling pt. Cake washed with 750 ml H ₂ O	336	26.0%	59.8	25.3	0.16	0.15	0.014
2	908	1 gal. of 2% NaOH 1 hr. at 80°C. Cake washed with 1000 ml H ₂ O	728	19.8	61.5	28.0	5.07	0.46	0.38
5	454	1/2 gal. of 2% NaOH 1 hr. at boiling pt. Cake washed with 750 ml H ₂ O	304	33.0	59.6	16.7	2.94	0.22	0.01-
6	454	1/2 gal. of 2.2% NaOH 1 hr. at boiling pt. Cake washed with 750 ml H ₂ O	292	35.7	58.9	18.3	3.78	0.24	0.005
7	908	1 gal. 20% NaOH 1 hr. at boiling pt. Cake washed with 1500 ml H ₂ O	635	30.1	61.5	17.9	2.55	nil	0.001

Table IB

Ether Extraction Tests

<u>Expt.</u>	<u>Dry Wt. sample (grams.) + adjust- ment material</u>	<u>Dry Wt. HNO₃ ins. (grams)</u>	<u>HNO₃ insoluble</u>	<u>Result</u>
3	276 + 50 grams sodium salt	192	58.9%	Stable Emulsion
2	164 + 90 grams sodium salt	148	58.2	Stable Emulsion
5	228 + 10 grams uranium oxide	189	78.4	Stable Emulsion
6	234	187	79.9	Stable Emulsion
7	300 + 30 grams uranium oxide	167	50.6	Stable Emulsion

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Table II

Carbon-sodium Carbonate Treatment of Vanadium Sludge

Expt.	Dry wt. sample (grams)	Comments on heating and leaching	Wt. dry leached cake (grams)	Grams V ₂ O ₃ in fil- trate	Quality Tests	
					Filtrate	Cake
9	50	2 hrs. at 500°C Filtrate volume 760 ml	31.6	8.07	+ V	+ V
10	50	1 hr. at 600°C 2 hrs. at 625-650°C Filtrate volume 1090 ml	23.3	9.5	+ V - U	? V + U
11	50	1 hr. at 700°C Filtrate volume 810 ml	25.4	10.9	+ V - U	- V + U
3	50	1 hr. at 800°C Filtrate volume 800 ml	24.8	11.2	+ V - U	- V + U
12	50	1 hr. at 800°C Na ₂ CO ₃ ·H ₂ O in- stead of Na ₂ CO ₃ Filtrate volume 800 ml	24.0	10.6	+ V - U	- V + U

Leached Cake

Expt.	U ₃ O ₈	V ₂ O ₃	SO ₄	Chloride	Sodium	HNO ₃ ins.	CO ₃ ins.
9	69.3%	8.9%	nil	0.089%	6.93%	3.79%	9.73%
10	85.4	nil	1.343%	0.029	1.67	8.33	5.93
11	83.4	nil	0.878	0.007	1.46	11.6	6.13
8	90.7	nil	0.871	0.027	1.25	4.23	5.3
12	88.8	nil	0.754	0.017	2.74	3.51	5.1

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