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CANADA

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**THE PREPARATION OF COMMERCIAL GRADE
VANADIUM PENTOXIDE FROM BOILER FLY
ASH SUBMITTED BY CANADIAN PETROFINA
LTD., POINTE-AUX-TREMBLES, QUE.**

by

J. A. VEZINA & W. A. GOW

EXTRACTION METALLURGY DIVISION

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THE PREPARATION OF COMMERCIAL GRADE VANADIUM PENTOXIDE
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J. A. Vezina* and W. A. Gow**

SUMMARY

A method has been developed for the preparation of commercial grade vanadium pentoxide from boiler fly ash submitted by Canadian Petrofina Ltd. Laboratory tests have shown that a sulphuric acid leach followed by the oxidation of the leach solution with sodium chlorate and the precipitation of the vanadium with ammonia will produce commercial vanadium pentoxide of a grade suitable for the production of ferro-vanadium alloys.

The overall recovery of vanadium was about 90 per cent and the chemical reagents consumption was about 3.5 lb H_2SO_4 , 0.25 lb $NaClO_3$ and 1 lb NH_3 per pound of recovered V_2O_5 .

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INTRODUCTION

This investigation was requested on behalf of Canadian Petrofina Ltd. by Mr. J.R. Patton, Vice President (Refining) in a letter dated March 27, 1963, following verbal discussions between Mr. W. Whigham, the company's chief chemist, and Mines Branch staff. In his letter, Mr. Patton asked for test work to explore methods of preparing saleable vanadium products from boiler fly ash produced at the company's refinery at Pointe-aux-Trembles, Quebec. At this plant, in the process for refining Venezuelan crude oil, petroleum coke containing a substantial quantity of vanadium is produced and is subsequently used as fuel for steam generation; the vanadium is thus concentrated in the fly ash from the steam plant.

Exploratory experiments were carried out and involved the application of soda ash, sulphuric acid and nitric acid for extracting the vanadium, and the preparation of various salts of vanadium by precipitation from the leach solutions with sulphuric acid, ammonia and ammonium chloride. Generally, the results showed that soda ash and nitric acid leaching produced solutions from which the vanadium was precipitated efficiently by adjustment to pH 2 with sulphuric acid or ammonia at a temperature of 80°C. Sulphuric acid leaching was different, in that it produced solutions from which the vanadium was not efficiently precipitated, by direct pH adjustment, apparently because of the presence of vanadium in a reduced state. It was shown, however, that the sulphate leach solution could be oxidized readily with either hydrogen peroxide or sodium chlorate. After oxidation the vanadium could be precipitated efficiently by pH adjustment as mentioned above.

The course of the investigation was oriented on the basis of the results of a survey conducted by the Mineral Resources Division of the Department of Mines and Technical Surveys, Ottawa. The survey showed amongst other things that the present demand for vanadium products in Canada is of the order of 160 tons annually and that about 74 per cent of this quantity is used for the production of ferro-vanadium alloys, for which a high purity vanadium product is not required. In view of the potential vanadium production of Canadian Petrofina Ltd., which may be in excess of 100 tons V_2O_5 annually, it was apparent that it was to the immediate advantage of this firm to aim for the production of a product suitable for the largest part of the market. Therefore, the program of the work reported herein was designed to develop a method for the preparation of a product suitable for the production of ferro-vanadium, i.e., containing a minimum 86 per cent V_2O_5 and a maximum 0.05 per cent phosphorus (1).

A series of preliminary experiments was carried out to determine the relative leaching properties of soda ash, nitric acid and sulphuric acid for the fly ash. The results showed that sulphuric acid was the most economical of the three media for leaching the vanadium from the ash.

From this information and known procedures for oxidizing and precipitating vanadium from sulphuric acid extraction solutions with ammonia, a flowsheet, shown in Figure 1, was conceived.

Finally, using the flowsheet of Figure 1 as a pattern, another series of 5 experiments was conducted to evaluate economical and practical conditions for leaching the fly ash, oxidizing and precipitating the vanadium as commercial vanadium pentoxide of grade suitable for the production of ferro-vanadium alloys.

PROCEDURE

Two shipments of boiler fly ash were received from Canadian Petrofina Ltd. These had been collected during June, July, August and September 1963 from the boiler chimney at the Pointe-aux-Trembles plant. Table 1 shows the results of chemical and semi-quantitative spectrographic analyses done on these samples.

The leaching of the ash was done in a covered glass kettle, electrically heated and equipped with a thermometer and a reflux condenser to maintain the volume reasonably constant. Liquid-solid separation after leaching was performed by filtration using a Buchner funnel. In the series of experiments for testing the flowsheet, the leach residues were repulped with boiling water, filtered and washed thoroughly again with boiling water. The filtrates from this repulping operation were not used further, but in practice they would be recycled to the head of the leaching step (Figure 1).

The vanadium in the extracted solutions was oxidized with sodium chlorate, added in crystalline form under agitation in open beakers, to the full change of color of the solution from deep blue to pale yellow; this change was rapid and in all cases occurred during a period of less than one minute.

The vanadium was precipitated in open beakers while agitating and keeping control of the temperature between 80-90°C and of the pH of the solutions between 1.9 and 2.1 with an automatic pH meter. The ammonia was added with a pipette, under the surface of the solutions, in the form of a concentrated solution in water.

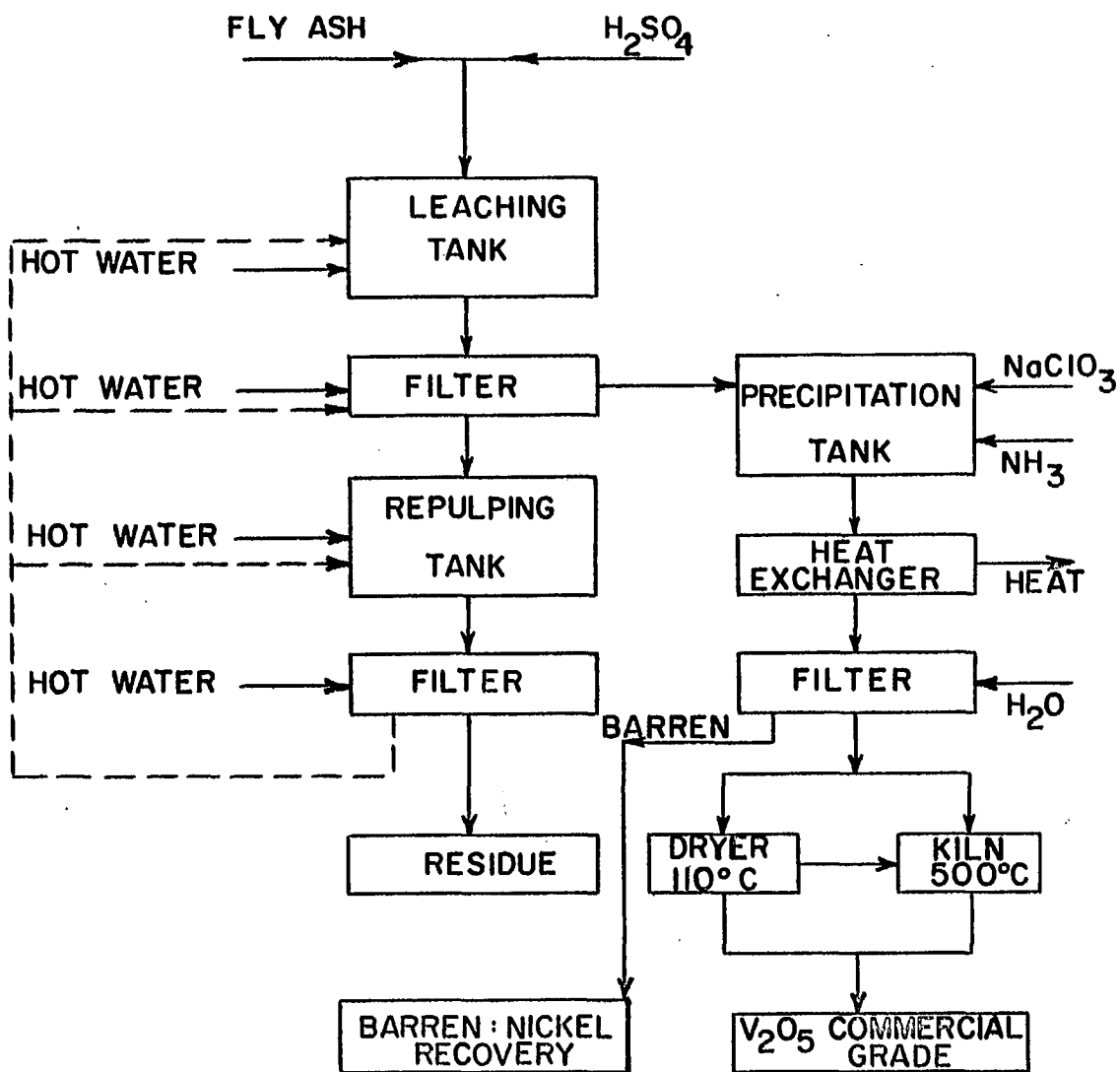


FIGURE 1: FLOWSHEET OF A PROCESS FOR THE PREPARATION OF COMMERCIAL GRADE V_2O_5 FROM FLY ASH SUBMITTED BY CANADIAN PETROFINA LTD.

TABLE 1

Analyses of Fly Ash Received from Canadian Petrofina Ltd.

1. Shipment received 6 August 1963, 2,180 grams
 2. Shipment received 24 September 1963, 657 "

Chemical, %

	V ₂ O ₅	Ni	Na	C	S	Fe
1	13.9	0.81	0.52	54	2.75	0.50
2	15.3	1.07	0.39			

Semi-quantitative Spectrographic, %

Si	Mn	Al	Pb	Mg	Ga	Mo	Ca	Zr	Ti	Co	Bi	Cr	Ag	Cu
3	0.007	2	Tr	0.1	Tr	0.01	0.3	0.009	0.2	0.1	Tr	0.002	Tr?	0.09
3	0.008	2	Tr	0.7	Tr	0.005	0.08	0.01	0.01	0.09	Tr	0.002	Tr?	0.09

A muffle furnace was used for drying and igniting the precipitate. The chemical reagents used were of reagent grade and the analytical determinations were done by standard chemical procedures.

RESULTS

The results of the preliminary tests done to determine the relative leaching efficiencies of soda ash, nitric acid, and sulphuric acid are given in Table 2. They have shown that the highest vanadium extraction was obtained in Test 7, when a large excess of nitric acid was used. It was thought, however, that the cost of extracting the additional 3.6 per cent vanadium above that extracted with a reasonable quantity of sulphuric acid, as in Test 8 for example, was prohibitive. The extractions with soda ash were not promising and were not considered further.

Of the three media tested, it appeared that sulphuric acid was the most economical for leaching the vanadium despite the fact that the vanadium in the sulphuric acid leach solution needed to be oxidized prior to precipitation; a step that was not necessary when sodium carbonate or nitric acid was used for leaching.

On comparing the results of Tests 8, 9 and 10 of Table 2, it is apparent that the quantity of acid used for leaching was a critical factor on the extraction of the vanadium. When the quantity of sulphuric acid used was reduced from 2.8 to 2.5g $\text{H}_2\text{SO}_4/\text{g V}_2\text{O}_5$, there resulted a decrease in the extraction of about 8 per cent, but when it was increased to 6.6g $\text{H}_2\text{SO}_4/\text{g V}_2\text{O}_5$, the extraction was increased by only 1.0 per cent. These results served as the basis for the selection of the quantity of acid used for all further tests reported in Table 3.

The results of five experiments carried out to test the proposed method of processing the vanadium from fly ash to a finished product have been recorded in Table 3. In these tests, the quantity of acid used was equivalent to 3g $\text{H}_2\text{SO}_4/\text{g V}_2\text{O}_5$ contained in the fly ash.

In Tests 1 and 2 of Table 3, the leaching conditions were based on those used in Test 8, Table 2, which produced a satisfactory and economical extraction of the vanadium; the leaching period was lengthened however to 24 hours in both tests. The two tests differed in that the temperatures of the solutions in the oxidation operation were set arbitrarily at 100°C and 70°C respectively in Tests 1 and 2.

TABLE 2

Results of Preliminary Leaching Tests with Fly Ash

Test	Fly Ash		Leaching Solution			Leaching		V ₂ O ₅ Distribution		Total as percent of head
	V ₂ O ₅ %	grams	Nature	g/l	g/g V ₂ O ₅ *	Temp °C	Time hrs	Filtrate %	Residue %	
1	13.9	50	aq. Na ₂ CO ₃	90	2.6	90	24	47.4	52.6	100.7
2	13.9	50	"	120	3.4	90	24	57.4	42.6	100.7
3	13.9	20	"	50	7.2	90	24	81.4	18.6	98.7
4	13.9	50	aq. HNO ₃	50	1.5	100	8	29.8	70.2	99.4
5	13.9	50	"	100	3.0	100	8	59.8	40.2	100.7
6	13.9	50	"	200	6.0	100	8	66.0	34.0	97.6
7	13.9	50	"	100	14.4	100	4.5	96.6	3.4	100.0
8	13.9	50	aq. H ₂ SO ₄	100	2.8	105	8	93.0	7.0	101.4
9	13.9	20	"	100	2.5	105	24	85.0	15.0	100.4
10	13.9	25	a) H ₂ O b) H ₂ SO ₄			90 105	16 8	} 94.1	5.9	
				210	6.6					

*Based on the vanadium content of the ash

TABLE 3

Record of Results Obtained from Tests for Developing a Process for the Preparation of Commercial Grade V₂O₅ from Fly Ash Submitted by Canadian Petrofina Ltd.

Test	Fly Ash			Leaching Solution aq H ₂ SO ₄			Leaching		Extracted Solution				Repulping			Residue Dry Weight as % of Ash
	V ₂ O ₅ %	Ni %	grams	g/l	$\frac{\text{g H}_2\text{SO}_4}{\text{g V}_2\text{O}_5^*}$	ml/g Ash	Temp °C	Time hr	Vol ml/g Ash	pH	Free H ₂ SO ₄ g/l	Spent H ₂ SO ₄ , g H ₂ SO ₄ g V ₂ O ₅ *	Vol ml/g Ash	Temp °C	Time min	
1	13.9	0.81	100	100	3.3	3.8	105	24	4.0				2.7	100	15	76.2
2	13.9	0.81	100	100	3.2	3.8	95	24	3.3				3.4	100	15	77.1
3	13.9	0.81	225	450	3.3	0.9	105	6	1.8	0.3	75.0	2.1	2.2	100	15	76.6
4	15.3	1.07	200	200	3.1	2.0	105	22	2.2	0.4	66.0	1.9	3.5	100	15	74.5
5	15.3	1.07	200	200	3.1	2.0	105	8	2.4	0.4	74.0	1.6	2.3	100	15	74.9

Continued

Test	Vanadium Distribution, %				Nickel Distribution, %				Total Extraction		Oxidation Step	
	Extracted Solution	Repulp Filtrate	Repulp Wash	Residue	Extracted Solution	Repulp Filtrate	Repulp Wash	Residue	%		NaClO ₃ , g/g V ₂ O ₅ *	Temp °C
									V ₂ O ₅	Ni		
1	93.1	1.6		5.3					94.7		0.26	100
2	93.0	1.8		5.2			11.5	94.8	88.5	0.23	70	
3	82.1	10.5	2.2	5.2	76.3	9.7	2	94.8	88.2	0.26	70	
4	85.2	7.7	1.9	5.2	79.5	7.4	1.5	94.8	88.4	0.20	50	
5	89.2	4.1	1.2	5.5	81	4.5	2.5	94.5	88.0	0.20	50	

Continued

Test	V ₂ O ₅ Precipitation				Precipitation Filtrate			V ₂ O ₅ Precipitation Efficiency, %	Overall Recovery, %	
	Temp °C	pH	Time, hr	NH ₃ , g/g V ₂ O ₅ *	Vol. ml/g Ash	V ₂ O ₅ , g/l	Ni, g/l		V ₂ O ₅	Ni
1	85	2	4	1.0	5.1	1.04	1.35	95.5	90.5	84
2	80	2	4	1.2	4.8	0.94	1.47	96.2	91.2	87
3	80	2	8	0.8	1.9	1.93		95.2	90.2	
4	80	2	4	0.8	1.7	1.82	2.40	96.0	91.0	83
5	80	2	4	1.0	2.2	1.67	3.13	96.8	91.5	84

* Based on the overall vanadium recovery

The vanadium extractions in these two tests were in agreement and the results showed that the repulping operation had scavenged an additional 1.7 per cent vanadium. The importance of the repulping operation is difficult to determine from a bench scale test, but it may well be that the cost of repulping and the additional filtering required would exceed that of the value of the vanadium recovered by this operation.

Tests 1 and 2, Table 3, showed that reducing the oxidation temperature from 100°C to 70°C had perhaps improved the vanadium precipitation efficiency and lowered the sodium chlorate consumption, but by amounts that are probably not significant at this scale of experimentation.

In Test 3, the leaching conditions were changed drastically to a low liquid-solid ratio of 0.9, a correspondingly high acid concentration of 450g H₂SO₄ per litre, and a shortened leaching period of 6 hours. This low liquid-solid ratio had the effect of making the pulp viscous and difficult to filter. The vanadium recovery in the leach filtrate was lowered, but the soluble losses in the primary filtration were recovered by repulping the filter cake with hot water and the total vanadium recovered from these conditions was near that of Tests 1 and 2. The high pulp density and acid concentration used in Test 3 had no significant effect on the sodium chlorate and ammonia consumption; the precipitation efficiency and the overall recovery were comparable to those experienced in the two previous tests of this series.

Finally in Tests 4 and 5, an intermediate liquid-solid ratio of 2.0 and a corresponding acid concentration of 200g H₂SO₄ per litre were selected for leaching, and the oxidation temperature was decreased to 50°C. The periods of leaching were 22 and 8 hours respectively.

The nickel and vanadium extractions in these two tests were similar, showing that increasing the leaching period beyond 8 hours had no beneficial effect in this respect. The results of the two tests were, however, different in that leaching for 22 hours consumed 0.3g H₂SO₄/g V₂O₅ more than that for leaching 8 hours only, an increase of about 10 per cent. This saving in sulphuric acid is apparent only, because later in the process, the residual acid in the leach solution is partly neutralized to pH2 with ammonia, for the precipitation of the vanadium. In fact, it is a matter of comparing the cost of leaching an additional 14 hours with that of a saving of about 0.2 lb NH₃/4 V₂O₅.

Reducing the temperature of the oxidation step to 50°C in Tests 4 and 5 was possibly the reason for the lower sodium chlorate consumption compared to that of the three previous tests of this series. Again, this saving is only apparent and for proper evaluation should be compared with the cost of cooling the leach filtrate to 50°C, and heating again to 80°C for the precipitation of the vanadium.

Decreasing the liquid-solid ratio of the pulp to 2.0 in Tests 4 and 5 had the effect of lowering the recovery of vanadium in the leach filtrate to 85 per cent and 89 per cent respectively, but as in the other tests, the soluble losses could be recovered by repulping in hot water.

The total vanadium recovered in each of the five tests averaged 90.7 per cent in the range 90.5-91.5. Considering that this variation is experimentally of little significance, and that the conditions of the oxidation step were varied widely, it appeared that the dominating factor for selecting conditions will depend on the relative capital and operating costs of the various procedures tested.

In all the leaching tests reported, the conditions of leaching were very corrosive, and in practice would necessitate special materials for the leaching vessels, filters and other process equipment. Because of the limited quantity of fly ash submitted, it was not possible to evaluate the engineering factors for the formulation of a complete process. It was however possible to show, using a small quantity of fly ash, that there was the possibility of lowering the temperature of the leaching to 70°C without loss of efficiency in the extraction of the vanadium. The effects of leaching at that temperature on the other operations of the method are not known, but there is no reason to believe that they should be affected adversely.

The nickel extractions and recoveries were quite uniform, but no attempt was made to process the precipitation barren solutions for nickel recovery at this stage of the test work.

The vanadium precipitates produced were dried at 110°C for about 16 hours and those from Tests 1, 2 and 3 were heated further to 500°C for 3 hours. The analyses of these products are shown in Table 4.

The results of Table 4 show that the ignited precipitate from Test 3 contained less than 86 per cent V_2O_5 and consequently may not be suitable for ferro-vanadium production. It also contained an excessive amount of sulphate, probably the result of leaching with high pulp density and high acid concentration.

The heated precipitates from the other four tests were within the V_2O_5 and P limits set by the U. S. Army and Navy Munitions Board(1) for commercial grade V_2O_5 used in the production of ferro-vanadium alloys, but it is possible that penalties may be levied against other contaminants such as sulphur.

It has been shown that an acceptable product can be prepared by drying the precipitates at 110°C, although they may be upgraded by about 8 per cent vanadium by heating further at 500°C.

TABLE 4

Analyses of Products Prepared from the Tests

Reported in Table 3, %

Test No.	1*	2*	3*	4	5
V ₂ O ₅	97.4	96.7	84.8	88.1	86.3
Fe	1.71	1.2	0.72	0.95	0.78
SiO ₂	0.1	0.1	0.1	< 0.1	0.1
Al	0.14	0.11	1.45	0.08	0.03
Na	0.08	0.18	0.25	0.11	0.14
S as SO ₄	0.09	0.14	3.52	0.17	0.25
Ni	0.064	0.064	0.10	0.05	0.044
P ₂ O ₅	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
NH ₃				2.7	3.1
L. O. I.				11.8	11.3

* Ignited at 500°C

DISCUSSION OF RESULTS

The test work has shown that sulphuric acid is preferable to nitric acid or sodium carbonate for leaching the vanadium from the Petrofina fly ash. Sulphuric acid effects efficient extraction of the vanadium and nickel at a low unit cost. In addition, the use of sulphuric acid presents advantages peculiar to Canadian Petrofina Ltd., in that this firm already uses sulphuric acid in the refinery operations and discards spent acid that possibly could be used for leaching the fly ash. A disadvantage of sulphuric acid is that under the leaching conditions tested it is quite corrosive and may present a problem in the selection of construction materials for leaching vessels and filtration equipment. However, in a test with a small quantity of ash, not reported here, it has been indicated that there was a possibility of reducing these conditions by leaching at a lower temperature.

It must be kept in mind that the results reported in Table 3 were those from tests carried out with gram quantities of ash and have served only to establish the feasibility of the proposed method. The results should be confirmed by larger scale testing to allow for the simulation and evaluation of practical operating conditions.

The test work has shown that the method tested was satisfactory from the views of chemical reagent cost and chemical efficiency in the recoveries of the vanadium and the nickel from the fly ash. The extractions and recoveries of the vanadium and nickel were strikingly similar in the five tests reported in Table 3 and it is reasonable to assume that the optimum reagent consumption and conditions were not obtained in the test work done. The method proposed and tested produced a grade of vanadium pentoxide of commercial value and suitable for use in ferro-vanadium production.

CONCLUSIONS

A method for the preparation of commercial grade vanadium pentoxide from boiler ash was developed and tested successfully at the laboratory scale; it is efficient and economical from the standpoint of reagents consumed. On the basis of the test work reported the conditions, for satisfactory treatment of the fly ash would involve leaching of the ash with 3.0-3.5g $H_2SO_4/g V_2O_5$, at a liquid-solid ratio of from 2.0-4.0 ml acid solution/g ash, at a temperature between 70-105°C for 8 hours. Following leaching and recovery of the vanadium-bearing solution from the insoluble material by filtration and washing, the solution would be oxidized

with about 0.25 lb NaClO_3 / lb V_2O_5 at a temperature of 50-80°C, then neutralized to pH 2.0 at a temperature of 80°C and incubated at this temperature for about 4 hours. The vanadium precipitate from the neutralization step would be recovered by filtration and dried and calcined.

This bench scale study has served to confirm the feasibility of treating Canadian Petrofina's boiler fly ash with relatively simple methods for the extraction and precipitation of the vanadium to produce a marketable product. It is recommended that the results obtained be confirmed on a scale simulating plant conditions from which reliable engineering data may be obtained.

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