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REMOVAL OF VANADIUM FROM A MAGNETITE CONCENTRATE SUBMITTED BY NORANDA MINES LIMITED

by

G. N. BANKS & R. A. CAMPBELL

EXTRACTION METALLURGY DIVISION

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REMOVAL OF VANADIUM FROM A MAGNETITE CONCENTRATE
SUBMITTED BY NORANDA MINES LIMITED

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G. N. Banks* and R. A. Campbell**

SUMMARY OF RESULTS

The possibility of removing vanadium from a magnetite concentrate containing an amount equivalent to 1.74 per cent V_2O_5 was examined. The results of laboratory experiments indicated that more than 75 per cent of the vanadium could be recovered from the concentrate in the form of a leach liquor. This was accomplished by mixing concentrate and sodium carbonate (19:1 by weight), pelletizing the mixture, roasting at $1300^\circ C$ in an oxidizing atmosphere for 1/2 hour, crushing to -100m size and leaching the fine product in hot water ($> 72^\circ C$) for 1 hour. The residue resulting from this treatment contained vanadium equivalent to 0.47 per cent V_2O_5 .

It was found that sodium carbonate was superior to either sodium sulphate or sodium chloride as a source of sodium ions for leaching by the above method, but further work is required to define the optimum conditions for maximum recovery of vanadium.

In experiments conducted to produce low-vanadium iron ore pellets it was found that, although the concentrate balled readily with or without added sodium salts, the compressive strength of the resulting fired pellets was relatively low. Leaching the fired pellets in hot water, to extract the vanadium, reduced the pellet strength still more. Pellets containing equivalent to 0.48 per cent V_2O_5 after leaching, were obtained when sodium carbonate was used as the additive; however the value of such pellets is difficult to predict. We know of no Canadian iron ores in which the vanadium content is reported. In the United States one ore used in the trade contains 0.68 to 0.70 per cent V_2O_5 but the tonnage produced is insignificant.

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INTRODUCTION

On June 20, 1960, about 100 lb of iron ore concentrate from Noranda Mines Limited, was received from the Mineral Processing Division. This contained vanadium equivalent to 1.74 per cent V_2O_5 . It was requested by the company that experiments be conducted to ascertain the feasibility of recovering the vanadium and producing a residue which would be saleable as iron ore.

In an Indian paper entitled "Studies on the Extraction of Vanadium Pentoxide from Vanadium-bearing Titaniferous Magnetite Ore", (N. M. L. Technical Journal, May, 1960), M. Roy and P. P. Bhatnagar indicated that 75 per cent of the vanadium could be recovered from vanadium-bearing titaniferous magnetite by roasting the material with sodium carbonate and then leaching in hot water. Evidence was presented that about 95 per cent of the vanadium in the leach solution could be recovered by precipitating it as sodium hexavanadate. This was accomplished by adding sulphuric acid to a boiling solution of the leach liquor. Because of the chemical similarity of the Indian titaniferous magnetite ore and the Noranda iron ore concentrate, it was thought that a similar method of extracting the vanadium might be successful with the latter material. The experimental extraction of vanadium from the Noranda concentrate by such a process is described in this report.

In each of the preliminary experiments the concentrate was mixed with sodium carbonate, sulphate, or chloride, and the loose mixture was roasted and leached in hot water to recover the vanadium. Later an investigation was made of the possibility of pelletizing the mixture and leaching the pellets to extract the vanadium, thus producing marketable low-vanadium iron ore pellets. In this latter work, particular attention was given to the effects of the various sodium additives on the strength of the agglomerates, and to the recovery of vanadium in the leach solution.

EXPERIMENTAL WORK

Roasting and Leaching Unagglomerated Concentrate

The chemical and screen analyses of the concentrate used in these experiments are given in Table 1.

TABLE 1

Chemical and Screen Analyses of Vanadium-bearing Iron Ore Concentrate

Chemical Analysis		Screen Analysis	
Constituent	%	Mesh Size	Wt % (Cumulative)
Total Fe	66.3	+100	0.8
Fe ⁺⁺	25.4	+150	3.8
V ₂ O ₅	1.74	+200	13.2
TiO ₂	3.96	+325	35.8
CaO	0.31	-325	64.2
SiO ₂	1.43		
MgO	0.60		
Al ₂ O ₃	2.76		
S	0.032		
P ₂ O ₅	< 0.5		

(1) Effect of Varying the Sodium Carbonate Content of the Mixture

Various proportions of concentrate and sodium carbonate were mixed to produce 200 gram samples. These were roasted for 4 hours at 950°C under oxidizing conditions in a muffle furnace. Each sample normally was rabbled every 15 minutes during roasting, although there were some variations in this procedure as outlined later. Each roasted product was weighed, pulverized to -100m and sampled. A 150g portion was placed in a beaker, water was added to give a volume of 500ml, and the material was leached at a temperature above 70°C for one hour, with constant stirring. The resulting material was then filtered, the filtrate was sampled, and the residue was dried at 120°C, weighed, pulverized to -100m and sampled. The results of these experiments are presented in Table 2.

In experiment No. 6, the mixture was roasted for 5 hours instead of 4 hours. In experiment No. 7, the mixture was not rabbled during roasting and the hot roasted material was dumped directly into hot water for leaching. The vanadium recovery in this experiment was based on the original weight and analysis of the concentrate; in all other experiments it was based on the weight and analysis of the roasted material. In experiments No. 8 and 9 a rotating furnace, rather than the muffle furnace, was used to roast the mixture, the roasting temperatures being 900°C and 850°C respectively.

TABLE 2

Results of Roasting with Sodium Carbonate and Leaching

Experiment No.	Additive		Leaching Temp (°C)	Analysis of Residue			Recovery of V ₂ O ₅ in Leach Liquor (%)
	Na ₂ CO ₃ (%)	Na (%) (calc)		Fe (%)	V ₂ O ₅ (%)	TiO ₂ (%)	
1	5	2.2	70	62.9	0.88	3.27	39.0
2	10	4.3	77	61.9	0.75	3.32	57.2
3	15	6.5	86	60.3	0.70	3.81	64.3
4	20	8.7	77	60.8	0.60	3.01	60.4
5	30	13.0	79	57.7	0.60	3.17	67.7
6	30	13.0	81	56.5	0.64	2.89	67.9
7	20	8.7	95	59.8	0.46	3.67	68.7
8	20	8.7	75	59.6	0.71	3.44	54.8
9	30	13.0	75	56.0	0.63	3.21	58.5

The results of the first five experiments show that for material roasted with rabbling in the muffle furnace, the recovery of vanadium in the leach liquor increased as the percentage of sodium carbonate in the mixture was increased. No benefit was obtained by using a longer roasting time (experiment No. 6 compared to experiment No. 5); and the material that was roasted without rabbling then hot quenched (experiment No. 7), gave a higher vanadium recovery than that which was rabbled during roasting and cooled before leaching (experiment No. 4). In this regard it will be noted that the leaching temperature obtained in experiment No. 7 was 18° higher than that obtained in experiment No. 4. The samples roasted in the rotary furnace (experiments No. 8 and No. 9) gave lower vanadium recoveries than those roasted in the muffle furnace; however, since the rotary furnace temperatures were lower, the results cannot be considered conclusive.

(2) Effect of Varying the Leaching Temperature

The effect of varying the leaching temperature, on the recovery of vanadium, was examined when sodium sulphate was used as the additive. The mixtures of concentrate and sodium sulphate were roasted in a muffle furnace for 4 hours at 950°C under oxidizing conditions, and rabbled every 15 minutes. Each roasted product was pulverized to -100m and divided into two equal portions. Each portion was leached at a different temperature. The results of these experiments, shown in Table 3, indicate that the recovery of vanadium was not greatly affected by increases in leaching temperature above 72°C. It is also evident that increasing the sodium sulphate content of the mixture from 5 to 20 per cent decreased the vanadium recovery.

TABLE 3

Effect of Varying the Leaching Temperature of
Roasted Concentrates Containing Sodium Sulphate Additive

Experiment No.	Additive		Leaching Temp (°C)	V ₂ O ₅ in Residue (%)	Recovery of V ₂ O ₅ in Leach Liq (%)
	Na ₂ SO ₄ (%)	Na (%) (calc)			
10A	5	1.6	72	0.87	43.0
10B	5	1.6	93	0.82	42.2
11A	20	6.5	84	0.88	32.2
11B	20	6.5	91	0.87	32.2

Roasting and Leaching Agglomerated Materials

(1) Roasting and Leaching Tablets

Before beginning an investigation in which pelletized mixtures were used, two experiments were performed with tablets made from a mixture of sodium sulphate and the iron concentrate. A number of 5/8 in. diameter tablets were made by compressing the mixture in a tableting machine under a one-ton load. These then were roasted at 950°C for 4 hours and sampled. One half of the tablets were leached in water, the remainder were roasted at 1300°C for 1/2 hour, sampled and leached in water. The results of these two experiments are outlined in Table 4. In experiment No. 12 the tablets disintegrated on leaching, whereas those tablets which were reroasted at 1300°C (experiment No. 13) remained intact on leaching.

TABLE 4

Results of Roasting and Leaching Tablets Containing Sodium Sulphate Additive

Exp No.	Additive		Roasting Temp (°C)	Leaching Temp (°C)	Chemical Analysis of Residue		Recovery of V ₂ O ₅ in Leach Liq (%)
	Na ₂ SO ₄ (%)	Na (%) (calc)			Fe (%)	V ₂ O ₅ (%)	
	12	20	6.5	4hr at 950	93	--	0.80
13	20	6.5	4hr at 950 plus 1/2hr at 1300	94	62.2	0.53	50.0

A comparison of the results of experiment No. 11 (Table 3), 12 and 13 (Table 4) indicates that compressing the feed material before roasting, and increasing the roasting temperature, increased the vanadium recovery in the leach liquor.

(2) Balling, Roasting, and Testing of Agglomerates

The object of these experiments was to study the effects of three sodium salts (carbonate, sulphate and chloride) on the pelletizability of this concentrate, the strength of the balls or pellets at various stages in the process, the recovery obtained in leaching the vanadium from the roasted pellets, and the vanadium content of the leached pellets.

In each of the following experiments 5000g of material (concentrate plus additive) was used. In the first experiment (No. 14) no salt was added to the concentrate. In each of the next three experiments, one of the sodium salts was mixed dry with the concentrate before balling. In each

of the last three experiments one of the salts was added to the concentrate as an aqueous solution during balling. The green balls, obtained in each of these seven experiments, were separated on punch plate screens into the following size fractions: $-1/2+7/16$ in., $-7/16+3/8$ in., and $-3/8+5/16$ in. A portion of each size fraction was removed for evaluation of the green strength of the balls, and the remaining balls were dried in an oven at 110°C . A portion of each size fraction was then removed for evaluation of the dry strength, and the remaining balls were fired at a high temperature to harden them into pellets and to cause the sodium salts to react with the vanadium-bearing minerals. In the firing procedure used, the balls were slowly heated ($2\frac{1}{2}$ hr) to 1300°C , held at this temperature for $1\frac{1}{2}$ hr, then allowed to cool slowly overnight. In one case (the $-3/8+5/16$ in. balls from experiment No. 18) they were held at 1300°C for 5 hr before cooling. A portion of each size fraction of the cooled pellets was removed for evaluation of their physical strength and for chemical analysis, and the remaining portion was leached in hot water, as explained under section 3 below.

The drop strength of each size fraction of the green and dried balls was measured by dropping 10 balls individually from a specified height onto a concrete floor and determining the average number of drops required to break or deform a ball. A height of 18 in. was used for green balls and one of 6 in. for dry balls. The compressive strength of each size fraction was measured on 10 balls or pellets individually in a modified sand core testing machine and the average load required to break or deform a ball or pellet was calculated. The strengths of the agglomerates in their green, dried, fired and leached states are tabulated in Table 5.

There was no discernible difference in the balling ease of the various mixtures in these experiments, but in most cases the sodium chloride additive gave a higher dry strength to the agglomerates, than either sodium carbonate or sodium sulphate additives. The highest fired compressive strength was obtained with $-1/2+7/16$ in. pellets containing 5 per cent sodium carbonate (experiment No. 15). The longer firing time in experiment No. 18 appeared to increase the fired strength of the pellets. In every case the compressive strength of the pellets after leaching was lower than that of the unleached fired pellets.

(3) Leaching Pellets for Recovery of Vanadium

In these experiments, 100g of fired pellets from each of the size fractions referred to in the preceding section of the report, were leached in 500 ml of hot water ($90 - 100^{\circ}\text{C}$) for 1 hour. The pellets then were separated from the leach liquor by filtering, dried and sampled for chemical analysis and strength tests. The leach liquor also was analyzed for its vanadium content. In experiment No. 15 and 18, samples of the $-3/8+5/16$ in. pellets were pulverized to -100m and -20m respectively before leaching. The results of the above experiments are outlined in Table 6.

TABLE 5

Strengths of Agglomerates

Exp. No.	Additive	Na		Moisture Content (%)	Screen Size of Balls (in.)	Drop Tests (drops/ball)		Compressive Strength (lb/ball or pellet)			
		(%)	(calc)			Green (from 18 in.)	Dry (from 6 in.)	Green	Dry	Fired	Leached
14	none	--	7.3	-1/2 + 7/16 -7/16 + 3/8	3.0	2.0	--	--	203.4	77.5	
					3.0	2.0	--	--	129.4	37.7	
15	5% Na ₂ CO ₃ (solid)	2.17	9.0	-1/2 + 7/16	2.8	2.6	2.4	4.5	248.6	161.0	
				-7/16 + 3/8	3.2	2.9	2.6	3.4	175.5	74.7	
				-3/8 + 5/16	--	2.8	--	75.0	32.3		
16	5% Na ₂ SO ₄ (solid)	1.55	5.9	-1/2 + 7/16	2.5	2.0	1.9	2.5	138.5	96.3	
				-7/16 + 3/8	2.4	2.0	1.7	0.8	185.6	118.9	
17	5% NaCl (solid)	1.97	5.8	-1/2 + 7/16	2.8	3.6	2.5	10.4	165.7	83.2	
				-7/16 + 3/8	3.1	5.4	3.1	9.5	154.3	61.2	
18	3.2% Na ₂ CO ₃ (solution)	1.38	7.1	-1/2 + 7/16	2.8	2.7	1.5	7.5	129.2	111.5	
				-7/16 + 3/8	2.9	3.3	1.6	4.8	102.9	52.1	
				-3/8 + 5/16	--	2.1	--	132.1*	77.2		
19	3.8% Na ₂ SO ₄ (solution)	1.23	9.1	-1/2 + 7/16	2.7	3.0	2.4	4.9	213.4	158.9	
				-7/16 + 3/8	3.0	3.0	2.0	3.7	185.6	114.0	
20	3.7% NaCl (solution)	1.45	6.3	-1/2 + 7/16	2.0	3.9	2.1	6.6	148.4	82.4	
				-7/16 + 3/8	2.3	4.4	2.2	8.2	176.4	69.9	

* Fired for 5 hours at 1300°C

TABLE 6

Results of Leaching of Pellets

Exp. No.	Additive	Na (%) (calc)	Size of Leached Pellet (in.)	Chemical Analysis of Residue (%)			Recovery of V ₂ O ₅ in Leach Liq (%)
				Fe	V ₂ O ₅	TiO ₂	
14	none	--	-1/2 + 7/16	63.2	1.50	3.96	5.5
			-7/16 + 3/8	63.3	1.45	3.56	5.5
15	5% Na ₂ CO ₃ (solid) ³	2.2	-1/2 + 7/16	63.3	0.70	3.66	57.8
			-7/16 + 3/8	63.1	0.56	3.59	68.0
			-3/8 + 5/16	63.4	0.48	3.77	72.1
			-100m	64.3	0.47	4.06	77.6
16	5% Na ₂ SO ₄ (solid) ⁴	1.6	-1/2 + 7/16	61.9	0.83	3.87	44.8
			-7/16 + 3/8	62.7	0.85	3.84	50.3
17	5% NaCl (solid)	2.0	-1/2 + 7/16	63.6	1.34	2.17	11.8
			-7/16 + 3/8	63.8	1.15	2.14	14.0
18	3.2% Na ₂ CO ₃ (solution) ³	1.4	-1/2 + 7/16	63.5	0.87	3.71	44.1
			-7/16 + 3/8	63.6	0.86	3.57	45.4
			-3/8 + 5/16	64.0	0.78	3.76	43.4
			-20m	64.4	0.71	3.87	51.3
19	3.8% Na ₂ SO ₄ (solution) ⁴	1.2	-1/2 + 7/16	64.0	0.91	--	43.6
			-7/16 + 3/8	63.2	0.82	--	47.9
20	3.7% NaCl (solution)	1.5	-1/2 + 7/16	65.8	1.32	3.61	10.6
			-7/16 + 3/8	63.8	1.12	3.67	23.4

Pelletizing the combination of concentrate and additive before leaching appeared to increase the recovery of vanadium. This is shown by comparing the results of experiment No. 1 (Table 2) with those of experiment No. 15, (Table 6). The results of experiments 15, 16 and 17 show that higher vanadium recoveries were obtained with sodium carbonate than with either sodium sulphate or sodium chloride. The results of experiment No. 15 indicate that the vanadium recovery in the leach liquor increased as the particle size of the material to be leached was decreased. The highest vanadium recovery was obtained when pellets containing 5 per cent Na_2CO_3 were ground to -100m before leaching.

DISCUSSION

Agglomerating before roasting and decreasing the size consist before leaching, appear to be the two major factors responsible for increasing the recovery of vanadium from this concentrate. The agglomerating procedure probably aids by giving more intimate contact between the sodium salt and the concentrate during roasting. Decreasing the size consist before leaching, probably aids by giving a greater area of contact between the roasted concentrate and the leach liquor.

The highest vanadium recovery obtained in these experiments was 77 per cent, resulting in a residue containing vanadium equivalent to 0.47 per cent V_2O_5 (experiment No. 15). Although the optimum conditions for treating the material by this procedure have not as yet been defined, it seems probable that higher vanadium recoveries could be obtained by increasing the proportion of sodium carbonate salt in the mixture. It has also been suggested that reroasting and releaching of the residue (either with or without additional salts) or longer leaching times might aid in increasing the vanadium recovery, but this has not been examined. The roasting conditions used in these experiments apparently were sufficiently oxidizing, since chemical analysis indicated that the ferrous iron content was reduced from 25 per cent in the unroasted concentrate to less than 1 per cent in the roasted material.

All of the vanadium recoveries reported in this investigation, except those of experiment No. 7, were based on the analyses of the roasted concentrates and the filtrates. Although subtracting the vanadium recovery in the residue from 100 per cent does not give the same results, due probably to slight variations in the chemical analyses, the trends observed by both methods are the same. Analyses of the roasted concentrates indicated that, in some cases, there was a loss of vanadium (about 10%) during roasting, but this also probably was due to slight variations in the chemical analyses.

D. D. Phelps and J. A. Anthes of the Dravo Corporation, in a paper presented at the AIME Blast Furnace, Coke Oven and Raw Materials Conference, April, 1962, discussed the specifications for iron ore pellets. They stated that, "the most common specifications given..... are a tumble result not exceeding 5 per cent -200m after 200 revolutions in an ASTM coke tumbler, compression strengths of 500 lb or more per pellet and a size consist of +3/8 -1/2 in." The maximum compressive strength of the fired pellets produced in these experiments was 249 lb, which is considerably lower than the above specification.

CONCLUSIONS

Although the optimum conditions for treating this concentrate to obtain the highest vanadium recovery were not defined, it can be stated that:

1. Vanadium recoveries were higher when sodium carbonate was used as a source of sodium ions than when either sodium sulphate or sodium chloride were used.
2. The recovery of vanadium increased as the percentage of sodium carbonate in the mixture was increased.
3. Higher vanadium recoveries were obtained when the mixture was agglomerated before roasting.
4. Higher vanadium recoveries were obtained when the roasted agglomerates were crushed before leaching.
5. Increasing the leaching temperatures above 72°C did not increase the vanadium recovery in the leach liquor.
6. Although the combination of concentrate and sodium salt can readily be agglomerated, the strength of the leached pellets is rather low and the -1/2 + 3/8 in. pellets (normally accepted blast furnace feed size) still contain about 40 per cent of the original V_2O_5 content after leaching. The acceptable upper limit of vanadium in iron ore is not known.