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REPORT

347

of the

ORE DRESSING AND METALLURGICAL LABORATORIES

Preliminary Tests on Treatment of
Titaniferrous Magnetite from Mine
Centre, Ontario, for Recovery of
Iron, Titanium and Vanadium Values

by R.J. Traill

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Preliminary Tests on Treatment of Titaniferous Magnetite from Mine Centre for recovery of iron, titanium and vanadium values.

By R. J. Traill.

Shipment: A shipment of 100 pounds of titaniferous magnetite marked M. G. 43, originally from the deposit at Mine Centre, Ontario, was received from W. M. Goodwin, Ste. Anne de Bellevue, Que. The ore was shipped from Kingston, Ontario, and was similar to that used in experiments on smelting carried out by W. M. Goodwin and reported by him in Report No. 8 (1921) to the Honorary Advisory Council for Scientific and Industrial Research. It contains small quantities of vanadium.

Purpose of Test Work: In the smelting process mentioned above, a pig-iron containing 90 per cent of the vanadium value was obtained, while the titanium value was lost in the slag. The possibility of recovering this titanium value in addition to the iron and vanadium was suggested by Mr. Goodwin and as a preliminary to a further and more complete study of the utilization of these ores to be undertaken by him, the following tests were carried out.

The process suggested was the one already carried out in this laboratory on ilmenite ores, embracing the low temperature reduction of the oxide iron to metallic iron, the separation of the metallic iron by dissolution in ferric chloride recovering the iron as electrolytic iron and obtaining the titanium and vanadium in the insoluble residue from the leaching. The main point to be determined is the behaviour of the vanadium and its concentration in the insoluble residue, followed by the separation and recovery of the titanium and vanadium values.

Experimental Work: A twenty pound sample was taken and crushed to pass an 8 mesh screen and a sample cut for screen and chemical analysis.

Screen Analysis.

<u>Mesh</u>	<u>Weight</u>	<u>Per Cent</u>	
+10	81.8 grams.	16.36	} 81.32 per cent.
+20	143.4 "	28.68	
+35	118.4 "	23.68	
+65	63.0 "	12.60	
+80	0.9 "	0.18	} 18.68 " "
+100	18.4 "	3.68	
+200	24.4 "	4.88	
-200	49.7 "	9.94	
	500.0	100.00	

Approximate Chemical Analysis.

Iron	48.38 per cent.
Titanium dioxide	12.82 " "
Vanadium pentoxide	0.86 " "
Silica	6.40 " "

The above analysis differs somewhat from that reported by Goodwin given as follows.

Iron	47.53 per cent.
Titanium dioxide	10.34 " "
Vanadium pentoxide	0.80 " "
Silica	13.93 " "

Metallization.

Metallization was carried out in an electric furnace of the heavy wire resistance type.

The containers for the charge were vitreosil muffles. Temperatures were measured within the furnace but not within the charge.

The charge consisted of:

Ore	970 grams
Coal	545 "
Coke	136 "

Four hours heating were required to bring the furnace temperature up to 1000° C with the temperature within the charge probably around 750° C. The furnace temperature was raised to 1050° C for five hours, the highest temperature within the charge probably being 50 to 100° below the furnace temperature. The weight of the reduced product was 1072 grams. Magnetic separation was carried out on the Ball Norton Belt concentrator, the products being:

Magnetics	725 grams.
Non-magnetics	347 grams.
Showing 67.5% magnetic product.	

Analysis of Magnetics.

Total Iron	-60.26 per cent.
Metallic Iron	-56.24 " "
Titanium dioxide	-16.52 " "
Vanadium pentoxide	- 1.08 " "
Metallization	-93.3 " "

The above test was duplicated, 1814 grams ore, 1090 grams coal and 272 grams coke being mixed and divided into two portions, placed in vitreosil muffles and metallized, using the same temperature range as previously. The results follow.

Weight of reduced product 1051 and 1060 grams respectively. The products were combined and passed over the magnetic separator.

Magnetics	1307 grams.
Non-magnetics	759 grams.
Showing 62% magnetic product.	

Analysis of Magnetics.

Total Iron	-61.21	per cent.
Metallie Iron	-58.34	" "
Titanium dioxide	-17.61	" "
Vanadium pentoxide	- 1.07	" "
Metallization	=95.3	" "

The non-magnetic tailing, analysed for V_2O_5 , showed 0.11 per cent. These results indicate no difficulty in obtaining good metallization of iron oxide in this ore and also show that about 90 per cent of the vanadium value and practically all of the titanium value is retained in the magnetics.

Leaching of Metallized Product.

Leaching tests of four litre volume leach liquor consisting of ferric chloride solution were made and the following tests are given as examples of the results obtained.

A metallized product analysing 60.26% total iron, 56.24% metallic iron, 16.52% titanium dioxide, was leached with four litres of ferric chloride solution containing 416 grams of iron. The charge of metallized product was 415 grams. Time of leaching was four hours. After filtration the liquor showed a small amount of unreduced ferric chloride.

The leach residue weighed 180 grams, showing 51.6% of the magnetic product as being dissolved. Analysis of the leach residue was:

Iron	13.59	per cent.
Titanium dioxide	33.93	" "

The extraction of metallic iron is approximately 90%.

Some hydrolysis was evident, amounting by calculation to about 3.5%.

Approximately 99% of the titanium is found in the residue.

A second test on 415 grams of metallized product analysing 61.21% total iron, 58.34% metallic iron, 17.61% titanium dioxide and 1.07% vanadium pentoxide was leached with ferric chloride containing 483.6 grams iron.

In this test reduction was complete in 30 minutes. The residue weighed 206 grams showing 50.3% of the charge dissolved.

The residue analysis was:

Iron	-	20.82	per cent.
Titanium dioxide	-	35.33	" "
Vanadium pentoxide	-	2.10	" "

The extraction of metallic iron figures out to 62%.

Hydrolysis occurred to a marked extent in this test, calculation showing an equivalent of 6%. This would account for so much iron in the residue. Over 99 per cent of the titanium and 97.7 per cent of the vanadium is found in the residue.

The interesting feature of these tests is the insolubility of the titanium and vanadium values in the ferric leach liquor and their retention in the residue. The value of this residue from the titanium recovery viewpoint is decidedly questionable. Even with higher iron extraction, or decrease of the amount in the residue, the value would not be materially increased as the undesired elements or gangue material amounting to approximately 33 per cent in the residue is too great.

Elimination of this gangue material from the ore would be beneficial, and would show increased titanium content in the residue. A separation is possible and is shown in this report.

The hydrolysis of the ferric liquor is probably due to the degree of neutrality of the liquor used and if so would be overcome with the addition of a small amount of hydrochloric acid in the leaching liquor.

Magnetic Concentration of Ore.

The possibility of magnetic concentration of the ore was looked into, mainly to determine if some of the gangue material could be removed without serious loss of titanium or vanadium values.

In the event that such a scheme is practicable, there would result a higher grade product to work with, and the leach residue obtained, after dissolution of the iron, would contain higher

vanadium and titanium values and lower interfering and troublesome gangue elements, with probably higher ultimate recoveries of titanium and vanadium.

The following is the result of a magnetic concentration test on the ore.

1000 grams -8 mesh ore passed over the Ball Norton belt separator.

Weight of magnetic concentrate	808 gms = 80.8%
Weight of non-magnetic tail	173 gms = 17.3
Loss in concentrating	19 gms = 1.9

Analysis.

<u>Head (Raw Ore)</u>		<u>Magnetic Conc.</u>	<u>Non-Mag. Tail</u>
Iron	48.38%	55.9%	21.00%
Titanium dioxide	12.85%	14.2%	7.51%
Vanadium pentoxide	0.86%	1.0%	0.27%
Insoluble residue	10.50%	4.06%	30.76%

The insoluble residue results are only approximate, but form a basis of comparison.

The magnetic concentrate was screened to pass a 14 mesh screen and the plus 14 mesh crushed sufficiently to pass 14 mesh and the whole again passed over the magnetic belt separator.

The result showed a further separation of 2.9% non-magnetic tailing. This result would indicate that some 20% of the weight of the ore can be eliminated with losses of approximately 5% vanadium, 10% titanium and 8% iron.

This magnetic concentrate, metallized and leached as proposed, should theoretically furnish a product well over 50% titanium dioxide and over 3.5% vanadium pentoxide, the remainder being gangue with a small amount of iron oxide. There is, however, the point to be considered as to how the increased fineness of the ore, namely minus 14 mesh, would effect metallization. From experience with ilmenite it has been found that the finer particles of metallic iron while hot oxidize very readily in contact with air. Finer grinding would also increase dust losses in any type of rotary or continuous operation furnace.

The value of this method could only be determined satisfactorily on a large scale operation plan. The above test, however, indicates and illustrates a possibility worth consideration and examination

Vanadium Recovery from Leached Residues.

Various methods have been suggested for the recovery of vanadium from ores. In general the processes comprise roasting with or without the addition of common chemical reagents, such as sodium chloride, sodium nitrate, sodium carbonate, sodium bicarbonate, fluorspar etc, followed by leaching of the soluble vanadates and subsequent precipitation as calcium or iron vanadate.

The following table shows some results obtained by roasting with various chemical reagents and leaching the soluble vanadate. The residue used for the charge contained 2.10% V_2O_5 .

Tests 1 to 4 were roasted in open dishes in the muffle furnace and test 5 was roasted in a combustion furnace with a slow current of oxygen passing over continuously. The result indicates that under oxidation is not the effective factor in the somewhat low soluble vanadate results obtained.

Test:	Charge grams.	Time Hrs.	Temp °C	Weight of Roast:	Charge: to Leach:	Leaching Medium	Volume Leach c.c.	V ₂ O ₅ in Leach Grams	Extraction %
1	25-Residue 4-NaCl 2-NaHCO ₃ 1-NaNO ₃	5	760-830	29.5	10 5 5	Water 4% NaOH 10% Na ₂ CO ₃	200 100 100	.1186 .0589 .067	66.6 66.2 75.2
2	25-Residue 4-CaF	5	760-830	29.0	10 5	Water 4% NaOH	200 100	.006 .0056	3.3 6.2
3	25-Residue 4-CaF 1-NaNO ₃	5	750-830	30.5	10 5	Water 4% NaOH	200 100	.006 .006	3.5 7.0
4	Same charge as 1	7 ⁵	710-830	28.5	10	Water	200	.087	47.8
5	25-Residue 4-NaCl 2-NaHCO ₃	5	800-900	29.5	10 10	Water 5% NaOH	200 200	.1048 .1108	58.8 62.2

A test to determine if time was a contributing factor to obtaining high solubility was run with the following results.

The charge consisted of 200 grams residue 24 grams NaCl 32 grams NaHCO₃ and was roasted in an open dish and hand rabbled. Samples were withdrawn at ninety minute intervals and the soluble vanadate determined.

<u>Sample</u>	<u>Time Roasted Hrs.</u>	<u>Temp °C</u>	<u>Soluble V₂O₅ on 5 gram sample</u>
1	1	750	0.058 grams.
2	2½	800	0.071 "
3	4	860	0.074 "
4	5½	875	0.074 "
5	7	870	0.079 "

The final roast contained 1.86% V₂O₅.

The above results indicate that after one hours roasting 55-60% of the V₂O₅ is soluble and this amount gradually increases with time until we find at the fifth sample some 65% of the V₂O₅ soluble in water. The combined residue from the five separate 5 gram samples treated with 4% Na₂CO₃ solution showed only an additional 3% of the total V₂O₅ dissolved.

A larger bulk leaching test of the above roast, consisting of 100 grams roast treated with 400 cc water for 5 hours gave 1.41 grams V₂O₅ in solution or 75.8%. The residue of 94.5 grams analysed 0.47% V₂O₅. Another sample of leach residue roasted with 20% salt alone for 7 hours showed only 56.8% extraction of V₂O₅ on leaching with water.

Present results, therefore, would indicate that the salt-sodium bicarbonate combination gives the better results in formation of soluble vanadate.

Leaching Raw Ore.

Some tests to determine the possibility of roasting the raw ore with various chemicals and obtain the vanadium in soluble form were tried with little success. Combinations of ore + NaCl + NaHCO₃ + NaNO₃, ore + CaF₂, ore + CaF₂ + Na₂CO₃,

ore + coal + NaCl + Na₂CO₃, ore + NaHCO₃ were used with varying results usually under 50% extraction. The ore + coal + NaCl + NaHCO₃ combination gave consistently higher results than the other combinations.

Finer grinding might assist in obtaining better results, but if the ore was crushed too fine it would be less suitable for further use in metallizing or other furnace treatment, and, therefore, further tests along this line were considered inadvisable.

Complete test on V₂O₅ Extraction.

The following compilation shows the vanadium and its occurrence in the various steps of the process under investigation.

The ore was metallized, the magnetics separated and leached with ferric chloride. The leached residue was next roasted with NaCl + NaHCO₃ and the soluble vanadate extracted with water.

<u>Product</u>	<u>Weight grams used-obtained</u>	<u>V₂O₅ %</u>	<u>Weight V₂O₅ used-obtained</u>
Ore	1814	0.86	15.60
Magnetic Product	1307	1.07	13.98
Non-Magnetic Product	759	0.11	.83
			<u>14.81</u>
Magnetica to leach	415	1.07	4.44
Residue from leach	209	2.08	4.36
Leached residue to roast	200	2.08	4.16
Roast	220	1.86	4.09
Roast product	100	1.86	1.86
Water leach			1.41
Water leach residue	94.5	0.47	0.44
			<u>1.85</u>

Conclusion.

Metallization of the iron content of this ore presents no difficulty. Muffle charges unrabbed have shown 95% metallization and with more suitable equipment such as a rotating kiln higher results should be obtained.

Leaching of the metallic iron with ferric chloride is readily accomplished, although in the tests carried out there is a disturbing iron hydrolysis factor, which has not been definitely traced to any special condition.

The ore carries a high gangue, which is found with the residue resulting from the dissolution of the iron with ferric chloride. The presence of this gangue materially reduces the value of the leach residue in terms of titanium and vanadium.

A magnetic concentration test on the ore shows that quite a large proportion of this gangue can be eliminated with but slight losses of titanium and vanadium. Such a magnetic concentration prior to metallization is, therefore, recommended in following out this process.

For recovery of vanadium from the ferric chloride leach residue, roasting with salt and sodium bicarbonate appears to give best results, 75% or over of the vanadium being obtained in a soluble form. Its recovery would entail precipitation with iron or calcium salts.

Treatment of the final residue for recovery of titanium has not been attempted, but the sulphate process should be adaptable. Recovery of the iron as electrolytic iron should present no difficulty as the ore seems to be free from the usual disturbing impurities.

The tests herein described are intended solely to determine the adaptability of this process treatment from a chemical or hydrometallurgical viewpoint and should be considered only as a basis to any future study that may be undertaken.

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