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July 25th, 1942.

R E P O R T

of the

ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1271.

Recovery of Vanadium from Dominion
Steel and Coal (DOSCO) Pig Iron.

TABLE OF CONTENTS

	<u>Page</u>
<u>Part I. - Notes on Dosco Steel Making Practice.</u> - - -	1
Raw Materials	1
Blast Furnace Department	3
Handling of Pig Iron	5
Open Hearth Division	5
<u>Part II. - Vanadium Recovery Experiments.</u> - - -	8
Ladle Tests	9
Experiments Involving Additions to Open Hearth and Mixer	19
Leaching Experiments on Vanadium- containing Slags	20
<u>Part III. - Review and Analysis of Possible Methods of Vanadium Recovery.</u> - - -	20
A. - Oxidation of Blast Furnace Taps	20
B. - Oxidation in Open Hearth and Mixer	25
C. - Oxidation in New Mixer	27
D. - Use of Basic Converter	28
E. - Use of Acid Converter	29
<u>Part IV. - Summary and Conclusions.</u> - - -	30



CANADA

BUREAU OF MINES
DIVISION OF METALLIC MINERALS
—
ORE DRESSING AND
METALLURGICAL LABORATORIES

DEPARTMENT
OF
MINES AND RESOURCES
MINES AND GEOLOGY BRANCH

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PART I. - NOTES ON DOSCO STEEL MAKING PRACTICE.

Raw Materials -

DOSCO smelt Wabana iron ores with Sydney coal. The iron ores are obtained from four mines. Ore shipped is generally a mixture from two mines. The mixture from one pair of mines generally contains about 2 per cent less silica than shipments of the mixed product of the other two mines. Because of this natural variation from shipment to shipment, and,

(Raw Materials, cont'd) -

indeed, from hold to hold on one ship, the blast furnace department is never positive of the silica content of the burden. This makes close control of pig iron analysis difficult. This situation has been accentuated because of shipping difficulties, as recently the Sydney plant has been operating on about an 8-day iron ore supply basis. This means that bottom is being scraped and extraneous matter may be picked up in loading iron ore. An early improvement in the shipping situation is anticipated, however.

The following is a typical analysis for Wabana iron ore:

<u>Iron,</u> <u>per cent</u>	<u>Silica,</u> <u>per cent</u>	<u>Phosphorus,</u> <u>per cent</u>	<u>Vanadium,</u> <u>per cent</u>
51.5-52.0	12.5-16.5	0.95	0.05

Cape Breton coke used in smelting this ore has the following composition: (Per cent) -

Fixed carbon	Volatile	Ash	Sulphur
91.50	1.00	7.50	1.80

It may be seen, then, that DOSCO are carrying out a very difficult metallurgical procedure, i.e. the smelting of high phosphorus ore with high sulphur coke. As a rule the high silica content of the iron ore would be a disadvantage, as it necessitates the carrying of a very large volume of slag and a consequent reduction of furnace capacity. It is true that this factor is in operation at Sydney, their 500-ton blast furnace being much larger than a furnace of similar capacity designed to operate on normal ores. The heavy slag volume, however, is an advantage as it reduces the problem of sulphur reduction (the large volume of basic slag carrying more CaS in solution). This

(Raw Materials, cont'd) -

is needed as the low manganese content of Wabana ore makes sulphur reduction more difficult (little fusible "MnS" forming).

Blast Furnace Department -

There are three blast furnaces in operation at Sydney and a fourth is being built, the old blast furnace shell at Ojibway being used in this construction. No. 1 Blast Furnace has a daily iron capacity of 500 tons. Blast Furnaces Nos. 7 and 8 are 350-ton units. The new furnace, which will be called No. 3, will be somewhat larger than No. 1.

In operating a blast furnace as a basic iron producer silicon control is important, as the open hearth department prefers low silicon iron for the silicon must be oxidized in the basic open hearth unit before other essential reactions can proceed. Low silicon iron can only be produced in a fairly cold furnace and furnace temperature cannot be kept too low or the sulphur content of the pig increases. In maintaining control, accurate knowledge of the burden composition is needed. When ore analyses fluctuate, as is the case at Sydney, silicon must be run rather higher in order to maintain a factor of safety as a high sulphur iron is useless.

Furnace design considerations may also affect the value at which the silicon content of the pig iron must be held, for the binder expands until it gets to 2100° F. where fusion brings about contraction and furnace design must be such that the point of maximum expansion does not occur at a constriction. Such a condition occurs when the heat is too localized in the tuyere area as a result of using too high a blast temperature. Bridging can be prevented by adding more coke to the charge (a practice that increases the silicon in the

(Blast Furnace Department, cont'd) -

iron) or by blowing steam in with the blast.

Conditions at Sydney are such that the silicon content of the pig must be held around 1.20 per cent, although it was said that Furnace No. 1 could make a slightly lower silicon iron. Before this latter furnace was relined bridging trouble was experienced and it was found necessary to blow steam in with the blast. The furnace operated very well under these conditions but after the furnace was relined this practice was abandoned, as it was said to be wasteful of coke. There is some evidence, however, that the greater part of the hydrogen produced when the steam was reduced by coke functioned as a reducer higher up in the stack with the result that the coke used to reduce the steam was not wasted. It is fairly certain, however, that unless steam is introduced into the blast the reduction of the present silicon content of the iron is impractical.

When the new blast furnace is finished one of the small furnaces will be blown out for relining. It is doubtful whether all four furnaces will operate at one time, as it was stated that there was not enough coke available for this.

A typical iron made in the No. 1 furnace has the following analysis:

<u>Carbon,</u> <u>per cent</u>	<u>Silicon,</u> <u>per cent</u>	<u>Manganese,</u> <u>per cent</u>	<u>Phosphorus,</u> <u>per cent</u>	<u>Sulphur,</u> <u>per cent</u>	<u>Vana-</u> <u>dium,</u> <u>per cent</u>
4.0	1.2	0.2	1.7	0.05	0.1

Practically all of the sulphur in the coke has been slagged off but all of the phosphorus in the burden and all of the vanadium enter the iron. The titanium in the iron is usually 1/10 of the silicon content.

Handling of Pig Iron -

Pig iron runs down runners lined with coke and silica sand into ladles which hold 40,000 to 45,000 pounds of iron. Usually, considering all three furnaces, there is a tapping every 1.5 hours but sometimes delay may increase this period to 2 hours. All of the iron for Melting Shop No. 1 (which contains the old small-sized units) is taken to a 500,000-pound basic lined mixer. Only a small amount of heat, in the form of two fairly weak coke oven gas flames, is added to this unit. There is little in the way of handling facilities in the mixer building. Iron is taken from this unit as required in the No. 1 shop. Materials handling in this shop is quite a problem as it only has one track and as a consequence charging of cold materials, charging of iron, and tapping are often in conflict. As a result, metal often cannot be added to the furnace at the exact time it is required.

The No. 2 shop (which is provided with the more modern large open hearth units) gets its iron directly from the blast furnace, as the mixer has capacity only for the No. 1 shop. Materials handling in the No. 2 shop is much better than in the No. 1 shop.

At the present time some additional pig iron is being made. This is going to the pig machine, as it will be required as soon as a new large open hearth is completed.

Open Hearth Division -

There are 10 old tilting-type basic open hearths (rated at 55 tons) and one basic lined electric furnace (rated at 10 tons) in the No. 1 shop.

The following melting practice is used:

Limestone is charged to the bottom of the furnace. This is covered with high-grade iron ore which is in turn covered

(Open Hearth Division, cont'd) -

with another layer of limestone. These materials are covered with scrap, heavy melting scrap being charged on the bottom. During a period of approximately 3 hours this scrap is melted down. When the bath becomes nearly level it is desirable to charge the pig iron. Sometimes pig iron is charged earlier owing to materials handling difficulties.

When handling permits, pig iron can be charged in 20 to 30 minutes. It was said that the pig iron - scrap ratio in the furnace was 70 to 30, which is unusually high. If handling conditions permit this to be charged at optimum time, i.e. when bath has just melted, the "run off" slag immediately forms. The furnace is tilted to allow this slag to run off. The slag can contain in the neighbourhood of 30 per cent silica and 10 per cent P_2O_5 , the oxidation of the phosphorus and silicon in the pig being effected by the FeO in the heat, the FeO coming from rust, etc., in the scrap. In spite of the high silica content of this slag, phosphorus enters it owing to the high phosphorus concentration. When iron addition is made at the right time, it does not take long to get over this run-off slag period. If iron is added before the bath is melted flat, as seemed to be usually the case, this run-off period may last 1.5 to 2 hours. The run-off slag, which is high in available phosphorus and incidentally contains 0.6 per cent vanadium, is run down into a box on the tapping side of the furnace. Soon after the "run-off" period the lime comes up from the bottom. The heat is then worked with additions of iron ore and fluorspar and from this point on the usual open hearth practice is followed.

The No. 2 shop contains four 125-ton basic open hearth furnaces and a fifth 125-ton unit is near completion. All furnaces are tilting. Practice is the same as in the

(Open Hearth Division, cont'd) -

No. 1 shop, save that it is less complicated by difficulty in materials handling. In this shop (No. 2) the run-off slag is collected in a box on the charging side of the furnace.

Incidentally, the two-slag practice is used, because it is believed every effort should be made to get rid of the phosphorus as soon as possible. This certainly seems to be sound logic as the phosphorus content in the pig is so high that P_2O_5 in the slag would probably build up to the point where mass action would prevent phosphorus removal if no slag were drawn early in the heat.

Two of the furnaces in the No. 1 shop were originally built as 300,000-pound acid-lined mixers. This was during the period when the company was operating basic converters and attempts were made to desiliconize in these mixers. Apparently the practice was never very successful, and it was said that the sulphur built up in the metal through the action of the high sulphur flame on the acid slag. Information given by Mr. F. E. Lathe (National Research Council, Ottawa) with regard to past operations indicates that this did occur. In any event, the company decided that the basic converter was uneconomic. However, in the comparison between the basic open hearth and the basic bessemer the latter practice was given an unfair advantage as the cost accountant charged the scrap it used at a very low figure. It is known that basic open hearth practice compares favourably with bessemer practice when scrap is low priced, but the latter practice usually has an advantage when scrap is high, all other things being equal.

All other things apparently were not equal at Sydney, however, for the company strongly holds that the converter is not more economic even when raw materials are fairly priced. This might be because of the high silicon, low phosphorus in

(Open Hearth Division, cont'd) -

the Sydney pig, for pig suitable for basic converter work should be low in silicon and high in phosphorus. Low silicon is required because for every part of SiO_2 in the slag, four parts of lime must be added to neutralize; consequently, high silicon means a heavy slag volume and loss of heat. High phosphorus is required because phosphorus is a fuel for the basic converter. It is not surprising, then, that the basic bessemer operation at Sydney was not too successful. Past experience has built up a strong opposition in the company to the use of any form of converter.

PART II. - VANADIUM RECOVERY EXPERIMENTS.

At present the vanadium in DOSCO pig iron is being oxidized into the open hearth slag. Any method of vanadium recovery must necessarily involve an oxidation of vanadium in preference, to a large extent, to the oxidation of other constituents of the pig iron.

DOSCO have been attempting to oxidize vanadium by adding mill scale to the ladle and ran some tests of this type as early as 1936. This year, about the first of July, a Plant Vanadium Committee was appointed. The personnel of this committee is as follows:

Mr. I. C. Mackie, engineer of tests,
Mr. Bower, Asst. Gen. Supt.,
Mr. L. Fulton, blast furnace department,
Mr. M. Campbell, open hearth department,
Mr. Theuerhauf, engineering department, and
Dr. N. Parlee, laboratory.

(Part II, continued) -

Ladle Tests -

This committee decided that all the scale in the plant should be used in the vanadium experiments. Results of experiments involving mill scale additions to the ladle follow. In so far as analyses of products are concerned, these results are none too complete.

Although tests have been carried out since June 24th, the results of this work have not been too closely controlled, the work being conducted mainly to develop a satisfactory teamwork and technique for the addition of scale to the ladle. No attention, then, has been paid to post-June 24th results.

(Table I now follows,
on Pages 10, 11 and 12.)

(Text is continued on
Page 13)

Table I. - Ladle Tests.

DATE	Wt.	Wt.	lb.	lb.	Ft.	Time	Time to	Wt.	ANALYSIS						
CAST	Pig,	Scale,	in	in	from	to	tap	slag	- (Per Cent) -						
NO.	lb.	lb.	ladle	runner	ladle	fill	cast,	recov-	REMARKS	Si	S	V			
FURN.	(Brkts,						minutes	ered,							
NO.	lb./100							lb.							
	lb. iron)														
Feb. 24/36 5683 #7									Pig B Pig A Slag	1.10 0.90	0.070 0.064	0.107 0.076	1.26		
Jan. 9/36 6320 #7	30,000 includ- ing scarp.	850 (2.8)		850			Seemed fas- ter and con- tinued longer than 1st time	50 (approx.) 10 40 standing.	336, some loss.	Ladle settled 1 ft. Two layers slag.	Pig B Pig A Slag T Slag B	0.40	0.264	0.093 0.065 0.97 1.06	Very high sulphur cast.
Nov. 5/41 6930		1350 (3.4)	250	500				60			Pig B Pig A Slag	1.32 1.02	0.012 0.015	0.61	Fe 34.24 (Snap samp.)
May 12/42 8045 #3	32,000	1800 (5.6)	800	1000	8		Very good. Some undis- solved scale in slag.	90	500 (approx.)	Two layers of slag.	Pig B Pig A Slag T Slag B	1.23 0.75	0.034 0.077		Snap.
May 26/42 8129 #8	45,000 (600 scrap partly included)	1350 ground partly dried (3.0).					Shoveiled in spout. Reaction not as violent as when using uncrushed.	60	1150 2 layers.	Two layers of slag 12" apart.	Pig B Pig A Slag R ^o	1.75 1.65	0.019 0.021	0.10 0.09 0.29	

^o R(good sample).

(Continued on next page)

Table I, Continued - Ladle Tests.

DATE	Wt.	Wt.	LB.	LB.	ft.	Time	Time to	Wt.			ANALYSIS			
CAST NO.	Pig.	Scale,	in	in	from	to	tap	slag			- (Per Cent) -			
FURNACE	lb.	lb.	ladle	runner	ladle	fill	REACTION	east,	recov-	REMARKS				
NO.		(Brackets				ladle		minutes	ered,					
		lb./100				in		in	lb.			Si	S	V
		lb. iron)				min.								
June 2/42 8169 #8	20,000 (?)	1800 (4.5?)	800	1000 (pushed in from inclined chute. #1 ladle.)	28		Good reaction. Geysers of liquid, boil- ing, etc., till ladle full.	75 (approx.)	1800	Two layers at first. Top fluffy and caved in.	Pig B Pig A Slag T Slag B Slag R	1.24 0.80	0.029 0.025	
June 3/42 8175 #8	42,000 (.415 M.A.)	1800 (4.3)	800	1000 Inclined chute.	41	10 (approx.)	Good reaction. As usual, spurs of flame through slag on freez- ing over.	60 (2505°F) (335 M.A.).	1000	Some layer- ing of slag but not pronounced.	Pig B Pig A Slag R	1.00 1.05 0.76 0.78	0.017 0.016	0.095 0.083 1.14
June 4/42 8181 #8	59,000 (?)	1800 (4.6?)	800	1000	41	5 (approx.)	Fair reaction but not as violent as June 3.	110 (.376 in M.A.)	Stuck ladle.		Pig B Pig A Slag R	1.58 1.12	0.028 0.021	0.103 0.083 0.65
June 15/42 8248 #8	42,000 (47,200?) .392 M.A.	1850 (4.4?)	950	900 Shoveled into spout. #1 ladle.	8	10 min.	Very noticeable.	60 Pig machine (.370 M.A.).			Pig B Pig A Slag R	1.57 1.18	0.026 0.009	0.76
June 17/42 8259 #8	40,000 (4,000 scrap) .396 M.A.	2100 (5.25)	1100	1000 From in- clined chute. Runner 1.	27	6 min.	Most violent yet. Lasted 3 minutes after ladle full. Some scale shoveled into spout.	145 min.	1000 Some stuck in ladle.		Pig B Pig A Slag R	1.17 0.89	0.071 0.074	0.76

(Continued on next page)

Table I, Concluded - Ladle Tests.

DATE;	:Wt. :	Wt. :	:Lb. :	:Lb. :	:Ft. :	:Time :	:Time to:	Wt. :	:	:	A N A L Y S I S			
CAST NO.;	:Pig,	:Scale,	:in :	:in :	:from :	:to :	: tap :	:slag :	:	:	- (Per Cent) -			
FURNACE NO.	: lb. :	lb. :	:ladle:	:runner:	:ladle:	:fill :	REACTION :	: cast, :	:recov-:	REMARKS :	:	Si	S	V
:	: (Brackets,	:	:	:	:	: ladle:	:	: minutes:	: ered, :	:	:	:	:	:
:	: lb./100 :	:	:	:	:	: in :	:	:	: lb. :	:	:	:	:	:
:	: lb.iron):	:	:	:	:	: min. :	:	:	:	:	:	:	:	:
June 19/42 8271 #8	40,000 (?)	2000 (5.0?)	1000	1000	41	8	No slag stuck in runner. Even flow. Good reaction. Lasted on surface 7 min. after fill.	68min. (to mixer).	600		Pig B Pig A Slag R	0.81 0.35	0.106 0.126	1.05
June 22/42 8289 #8	38,000 (?) .403 M.A.	1600	1100	500	27	3	Good reaction. Surface quickly froze but reaction below was very noisy.	40min.		Vigourous reaction up to casting time.	Pig B Pig A Slag R	1.54 1.34	0.031 0.016	0.68
June 24/42 8302 #8										Samples, average 4 ladles.	Pig B Pig A Slag R	1.04 1.07 0.62	0.017 0.012	0.78

(Ladle Tests, cont'd) -

It is evident that the slag recovery has not been too good, and a better conception of the reactions would have been gained had more analyses been taken. Apparently, full analyses were only made on the products obtained in the tests of February 24, 1936. Analyses of these products follow:

Table II.
Analysis of Products (in per cent)

	Fe	Si	Mn	V	Ti	P	C	S	CaO	MgO	SiO ₂
Pig B -		1.10	0.25	0.107	0.108	1.71	3.46	0.070			
Pig A -		0.90	0.23	0.076	0.084	1.64	3.49	0.064			
Slag -	35.98		4.71 [Ⓢ]	1.26	1.04	0.51		0.11	1.30	0.08	38.30

[Ⓢ] This value seems erroneous. In view of the low manganese content of the burden it should be under 1 per cent.

The first test, then, showed that vanadium could be concentrated in the slag but sufficient data were not collected to make possible a recovery calculation. Subsequent tests confirmed the findings of this first test and indicated that an addition of 4.5 pounds of scale to 100 pounds of iron resulted in a silicon reduction of approximately 0.40 per cent. Oxidation in the ladle apparently cannot be increased much by adding more mill scale, as the tests of June 17th, with larger additions, did not produce very much greater silicon oxidation. Apparently, then, the area of slag metal interface and the time allowable limit the amount of oxidation that can be obtained. Indeed, it is possible that oxidation equivalent to an 0.4 per cent silicon

(Ladle Tests, cont'd) -

reduction could be effected with a smaller scale addition. If this should be the case it would be better to add less mill scale as this would involve less dilution of the vanadium. (It might be argued that slag equilibrium is established and that any excess FeO added would be reduced to iron and consequently be an effective oxidizer. The fact that silicon does not appear to drop with the increased addition of scale would appear to contradict this assumption.) This does not rule out the possibility that an approximate equilibrium may be established with additions of scale of the order of 4.5 pounds of scale per 100 pounds of iron and for scale additions of less than this amount.

Vanadium content of the slag fluctuates considerably. It is thought that this indicates variation in slag dilution rather than variation in vanadium recovery. For instance, consider the test of June 2, 1942, when slag collection was apparently better than usual. Silicon reduction in this instance was 0.44 per cent. On the basis of 40,000 pounds of pig iron in the ladle, this represents a silica formation of 383 pounds. If the silica content of the slag were nearly similar to that in the slag produced in February 1936, the 1600 pounds of slag would contain approximately 600 pounds of silica. Even if slag recovery had been 100 per cent, which certainly was not the case, the silica pickup for this test would be in the order of 200 pounds. This silica could come from the binder material and the coke-ash in the runner and runner dams, from floor sand, from blast furnace slag, and from refractories, and there is no reason to suppose that this dilution would be constant.

(Ladle Tests, cont'd) -

Again referring to the test of June 2nd, it may be seen that the slag contained 37.85 per cent iron (48.7 per cent FeO). On basis of slag analysis made in 1936, it may be concluded that the slag from tap 8167 would approximately contain the following:

<u>FeO,</u> <u>per cent</u>	<u>MnO,</u> <u>per cent</u>	<u>V,</u> <u>per cent</u>	<u>Ti,</u> <u>per cent</u>	<u>CaO,</u> <u>per cent</u>
48.7	1.0	0.87	0.67	1.30

If the silica content of this slag were around 40 per cent, this would account for 94 per cent of the slag. The additional 6 per cent can be accounted for by reasonable variations, such as additional blast furnace slag, additional oxygen for metals present, etc. Consequently, it can reasonably be supposed that a silica content of approximately 40 per cent can be assumed for the ladle slag.

Unfortunately, lack of accurate data on slag weight and slag and metal composition makes it impossible to calculate recovery. However, an approximation of recovery may be gained by the use of the following formula:

Total slag weight = scale added + silicon reduced + silica pickup + oxides other than those of iron and silicon - iron reduced to slag.

Putting slag weight equals X, knowing scale charge to be 1800 pounds, silicon reduction to be 0.44 per cent on 40,000 pounds of iron, assuming the silica content of the slag to be 40 per cent (which makes silica pickup equal to $40X$ - silica formed from silicon oxidized), knowing the iron in the slag to be 38 per cent and the iron content of the scale

(Ladle Tests, cont'd) -

to be 70 per cent, and assuming extraneous oxides equal to 5 per cent (a fairly logical figure, in view of the 0.89 per cent of vanadium present), the formula would equate as follows:

$$X = 1800 + 176 + (.40X - 380) + .05X - (1260 - .38X),$$

from which, $X = 1980$ pounds.

This figure is merely an indication of the weight of the slag that would be recovered as it is considerably affected by the silica content of the slag and the amount of oxides other than those of iron and silicon that may be present. The figure, however, must be reasonably near the correct one, although it is probable that the actual slag weight was somewhat less, as the non-silicon iron oxides would probably be more than 5 per cent.

As the significance is only to two figures, and the probability is that the value of X was lower, it will be assumed that the slag weight was 1900 pounds. In this event, silica pickup equals 380 pounds, iron reduced to the slag equals 576 pounds, and the per cent of vanadium oxidized to the slag would be 41 per cent ($.0087 \times 1900$ divided by 40). Actual vanadium recovery, because of difficulty in slag collection, was 35 per cent ($.0087 \times 1600$ divided by 40).

The calculation indicates that about 45 per cent of the iron in the mill scale is reduced. This would mean that in calculating the oxidizing power of Fe_3O_4 it should not be regarded as releasing only one oxygen but, instead, one plus $.45 \times 3$, or 2.35 oxygens.

The above calculations are, of course, quite artificial, because they are based on only one test and many

(Ladle Tests, cont'd) -

assumptions. They have been merely recorded in an effort to obtain some rough approximation of the vanadium oxidized to the slag, the silica pickup, and the efficiency of the oxidizing addition. A slag analysis would make possible an exact calculation, as then no assumptions need be made.

It would seem advisable, then, to analyse slags on hand as it would thus be possible to get some exact data on the relative oxidizing powers of oxides that are available for this work. For instance, if 45 per cent reduction of the iron in iron oxides can be assumed, this would mean that Fe_3O_4 and Fe_2O_3 would respectively release 2.35 and 1.90 oxygens per gram molecule. Were MnO_2 to be used as an oxidizer only one oxygen would be released per gram molecule as there would be little reduction of MnO . Sodium nitrate, one of the most violent oxidizers, would release 2 oxygens per gram molecule. On the above assumptions the relative weight of oxygen released per 100 pounds of oxide would be:

$NaNO_3$	-	37	pounds
Fe_2O_3	-	19	"
MnO_2	-	18.4	"
Fe_3O_4	-	16.2	"

Sodium nitrate probably could not be used, as it would be too hard on the refractories. There is not much difference in the oxidizing powers of the other three oxides, but very high grade iron ore should be the best addition agent (on the basis of 45 per cent reduction of its iron contents). It should be remembered, also, that the slag must establish an equilibrium, or an approximation to an equilibrium, with the iron. This means that the slag must carry a fair amount of FeO . If this FeO is not supplied in the addition agent, it must be

(Ladle Tests, cont'd) -

oxidized from the iron. Oxidation of this iron from the valuable pig by air blowing would not be economic. Taking everything into consideration, then, a very high grade iron ore or mill scale appears to be the best possible oxidizing agent. In view of the difficulty of obtaining the former product and the availability of the latter, it would appear probable that mill scale will prove to be the most satisfactory oxidizing agent.

During the visit to Sydney, additional experiments were made with ladle additions. Ladle slag from a previous run (presumably containing around 1 per cent vanadium) was used as an oxidizing agent for a second tap, the object being to obtain a slag higher in vanadium. Results of this test are not yet available, but it is not expected that they will be too good, as the ladle slag lacks oxidizing power. A 500-pound addition, consisting of equal parts of soda ash and saltpetre, was charged to the ladle. Results obtained were very poor, the resulting slag being low in vanadium (0.03 per cent) and high in carbon (14 per cent). In addition, the ladle lining was badly attacked and the mixture gave off objectionable fumes when added to the iron. An attempt was made to aid oxidation by blowing air into the metal. Difficulty was experienced in developing a satisfactory air pipe. A refractory-cased iron pipe broke off in test. Indications were, however, that the small volume of air introduced acted well, for the ladle used contained a skull prior to receiving a test tap and the skull was melted away in the vicinity of the air pipe. If no luck is had with refractory-cased pipe, a graphite-cased pipe will be tried.

Experiments Involving Additions To Open Hearth and Mixer -

No attempt has been made to concentrate vanadium in mixer or open hearth slags, though this may well be possible, as the present "run-off" slag from the open hearth contains 0.6 per cent vanadium. It is hoped that the open hearth department will give permission to make the following tests:

TEST 1. - Melt scrap to level and charge iron as fast as possible. To this pig iron add high-grade ore in the ratio of 5 pounds ore to 100 pounds iron. As this addition would eventually overoxidize the bath, the weight of the material added must be subtracted from the weight of the ore originally charged to the bottom of the bath.

It is hoped that the iron ore addition will oxidize the silicon and vanadium and that the slag produced will be sufficiently high in silica to prevent too much P_2O_5 concentration. It is planned to withdraw this slag in about 30 minutes.

Test 2. - As in Test 1, save to add additional silica to reduce phosphorus concentration in slag. This high acid slag would, of course, attack the dolomite backs, so that the time it could be left in the furnace would be limited.

Tests in the present mixer appear to be out of the question, as the mixer's shop has very little facilities for test work and the testing might interfere with the steel production of No. 1 Shop. In any event, only half the iron can be treated, as the capacity of the mixer is only sufficient to handle metal for the No. 1 shop (in the month of June, 15,741 tons were treated in No. 1 Shop and 12,650 tons in No. 2 Shop, additional iron produced being pigged).

It might be possible to convert either the A or the B furnace of No. 2 Shop to a 500-ton acid lined mixer and to reduce the silicon and vanadium in the pig by carrying a high oxidizing charge in this mixer. It is doubtful if the company would allow such a change, as it would involve the loss of one of their large open hearth furnaces.

Leaching Experiments on Vanadium-Containing Slags -

Dr. N. Parlee has been running some small-scale leaching tests on slags. He first roasted a mixture of 15 per cent sodium chloride, 5 per cent sodium carbonate and 80 per cent slag and then leached the roasted product. Mr. Lathe reports recovery of vanadium by this method to have been 70 per cent. On one test, however, 0.73 per cent vanadium out of 0.93 vanadium in the slag was recovered. This represents a recovery of about 80 per cent, which is of the order that the literature on the subject would lead one to expect would be achieved. Dr. Parlee has found that the best roasting temperature is 800° C. and that best extraction is obtained when the products are ground to minus 200 mesh.

PART III. - REVIEW AND ANALYSIS OF POSSIBLE METHODS OF VANADIUM RECOVERY.

A. Oxidation of Blast Furnace Taps -

In this method the iron can be oxidized either in the ladle or in a separate reaction box. Various oxidizing agents may be used. The following have been suggested: mill scale, high-grade iron ore, high-grade manganese ore, soda ash, sodium nitrate, and air. The experimental work, while not sufficiently extensive to permit of any definite conclusions, would indicate that mill scale or high-grade iron is the best oxidizer (see Part II, pages 17-18) and that if the oxide is added to the ladle and not to a separate reaction box about a third of the vanadium can be recovered by this method (Part II, page 16).

Blowing air into the ladle has interesting

(Oxidation of Blast Furnace Taps, cont'd) -

possibilities. At first sight it might be thought that if this method were used a higher grade of slag would be produced, as the vanadium would not be diluted by the oxide addition. This conclusion, of course, is highly superficial, as the slag will take up an iron oxide content in accordance with the equilibrium, or approximation to equilibrium, existing at the time. As pointed out in Part II, it would not be good practice to get this iron oxide for the slag from the fairly expensive pig iron.

Howe, in the Journal of the Iron and Steel Institute, 1890, vol. 11, page 102, gives the following values for converter operation, starting with an iron of the following composition:

<u>Carbon,</u> <u>per cent</u>	<u>Silicon,</u> <u>per cent</u>	<u>Manganese,</u> <u>per cent</u>	<u>Phosphorus,</u> <u>per cent</u>	<u>Sulphur,</u> <u>per cent</u>
3.10	0.98	0.40	0.101	0.06

<u>Time of</u> <u>blow, in</u> <u>minutes</u>	<u>Silicon content</u> <u>of metal,</u> <u>per cent</u>	<u>Silica content</u> <u>of slag,</u> <u>per cent</u>	<u>FeO content</u> <u>of slag,</u> <u>per cent</u>
2.0	0.63	42.20	40.29
3.2	0.33	50.26	34.24
6.3	0.03	62.54	21.26
8.6	0.03	63.56	21.39

At a stage in the blow when the silica content of the slag reaches 40 per cent, therefore, the FeO content on the straight blow is also 40 per cent.

Slags produced by adding an oxide to the blast furnace ladle contain about 40 per cent silica but slightly higher FeO content (around 49 per cent). The difference, however, in converter and ladle conditions is not marked and

(Oxidation of Blast Furnace Taps, cont'd) -

probably indicates a departure from equilibrium conditions in the ladle as a result of restriction of reaction surfaces.

Increase in grade produced by straight blowing, then, would be slight. The blowing method would involve the difficulty of maintaining blowing pipes and the possibility of some attack on the ladle lining if oxidation in the ladle should be sufficiently marked to cause a high temperature rise. On the other hand, it might (providing the iron oxide for the slag were satisfied with mill scale additions) offer a cheap and convenient method of oxidation.

One attractive feature of the blowing method, which is in reality an attempt to apply the bessemer procedure, is that its use might make possible (in the event that above-mentioned difficulties did not interfere) a better recovery of vanadium. Apparently, vanadium recovery is limited in the ladle addition method, as heavier scale additions do not produce more severe oxidation because of the limitation in reaction surfaces (Part II, page 14). The blowing method could be carried on until all vanadium was oxidized. Whether or not it would be necessary to oxidize all the silicon to achieve this is not known. The literature indicates this to be the case but results obtained at Sydney show that substantial vanadium oxidation occurs with only a percentage of the silicon oxidized. It may be that the relative oxidation of the two elements is effected by temperature. If vanadium oxidizes better at a lower temperature the largest effective amount of mill scale could be added. If high temperature promotes preferential vanadium oxidation (which seems unlikely), only the amount of ferrous oxide required for slag equilibrium

(Oxidation of Blast Furnace Taps, cont'd) -

should be added as scale.

It has been suggested that all blowing could be done on one site, that the blowing equipment could consist of a cover through which blowing pipes would protrude, and that air could be obtained by tapping the No. 1 Blast Furnace air line.

The No. 1 Blast Furnace blower furnishes air at 18 to 20 pounds pressure and has a capacity of 60,000 cu. ft. At present this unit is only delivering 45,000 to 50,000 cu. ft. of air, so blast furnace conditions could be maintained on a tapped line by stepping up air delivery. A spare turbo-blower capable of delivering 35,000 cu. ft. at 18 pounds pressure is available for experimental work.

The above method looks fine on paper but maintenance and materials handling problems would be great. In addition, considerable construction would be involved, and the number of ladles would have to be increased by 50 per cent, as the ladles could only be two-thirds filled owing to the splashing which would occur on blowing. An arrangement involving both blowing and mill scale additions would seem to have possibilities, as it would give a greater reaction surface than the straight scale addition method and consequently increase the vanadium recovery.

According to calculations made in Part II (pages 15 and 16), about 400 pounds of silica is introduced with the scale as a result of attack on runners and ladle and extraneous additions of coke and blast furnace slag. This material not only dilutes the slag but also cuts down the efficiency of the oxidizing agent, for FeO must establish an equilibrium, or near equilibrium, with the silica. When additional silica is

(Oxidation of Blast Furnace Taps, cont'd) -

added, the amount of FeO required for equilibrium is therefore increased, with the result that it is lost as an oxidizing agent. Reduction of the silica in the slag, then, would not only improve the grade of slag but also increase the efficiency of the oxidizing agent.

Tramp silica additions to the slag could be largely prevented if the iron were not oxidized in the ladle but in a reaction box. The iron could be poured into this box from one ladle, oxidized, and then charged to another ladle for delivery to the open hearth department. Heat produced in the oxidation would prevent the iron from getting cold. The method would have one further advantage in that the oxidizing agent could be added more easily than it could to the blast furnace tap. In addition, the present method of ladle additions involves iron loss, as the open hearth operator does not like to pour the ladle clean owing to the presence of so much slag.

American Rolling Mills are said to be using a reaction box for desiliconizing their pig iron. It might be that this type of box would be ideal for the vanadium oxidation. It is hoped that this unit will be seen shortly. Kjelling (Engineering and Mining Journal, 123, pp. 521-22, 1927) also mentions a box-type unit in which he produced a very high grade of vanadium slag from vanadium-containing pig iron. The desiliconizing of the pig should not only lead to vanadium recovery but should also improve steel production, as the open hearth furnaces should operate more rapidly on the lower-silicon iron.

Prevention of dilution of slag might be expected to raise the vanadium grade from 0.87 per cent to 1.1 per cent (on

(Oxidation of Blast Furnace Taps, cont'd) -

the assumption that 400 pounds of silica would be kept out of the slag--Part II, page 16). It should be emphasized, however, that so long as the silicon in the pig iron is high (which seems inevitable--Part I, pages 3-4) the grade of slag produced in either the ladle or the reaction box will be comparatively low, as the vanadium will almost certainly be diluted by the large portion of the silicon present in the iron. It would seem to be the best procedure to treat this low-grade material, but in the event that this should prove uneconomic a better grade material could be obtained by recirculating the slag through one blast furnace or by reducing the slag in the 10-ton electric furnace. In the latter method the iron and vanadium could be reduced and the silica slagged off, after which the pig produced could be given an oxidizing treatment. This procedure would not appear to be practical, as there would be difficulties in reducing oxides in a melting unit and as the procedure would involve the loss of a furnace which is now making specialty steels on a 24-hour basis. Probably, however, it could be operated to effect separation of any phosphorus that may have followed the vanadium.

B. Oxidation in Open Hearth and Mixer -

In present practice all vanadium is being oxidized in the open hearth but in an unusable form (low-grade vanadium, high-phosphorus slag). It has been suggested that the open hearth procedure could be so controlled that vanadium and silicon could be fairly efficiently oxidized to the slag immediately after the pig iron additions to the open hearth, the oxidation being effected by iron ore additions.

It is claimed that the method would allow for more effective oxidation than ladle or reaction box methods, as heat

(Oxidation in Open Hearth and Mixer, cont'd) -

could be supplied to aid in the oxidation. Little additional equipment would be needed should this method prove successful. It would also involve practically no interference with present practice as two slags are now being drawn from the open hearth furnace.

The above logic is sound, although additional heat may probably not favour preferential vanadium oxidation, but the inability to handle materials satisfactorily in the No. 1 Melting Shop (Part I, page 5) and the problem of phosphorus make questionable the merit of the method. As pig iron cannot be delivered exactly as required in the No. 1 Melting Shop, fast accurate slag reactions are out of the question. The open hearth method, then, cannot be used for the smaller open hearth units.

Vanadium content of open hearth slag produced by this method would be fairly low. Consequently, recirculation through the blast furnace would probably be necessary. It has been suggested that difficulties in applying the method in the No. 1 Shop could be overcome by the following procedure: Use the method described above in the No. 2 Melting Shop. Recirculate the slag produced through one blast furnace and make sure that all the pig produced during this recirculation period is fed to the mixer that serves the No. 1 Shop. The vanadium content of the mixer metal could then be oxidized to slag by oxide additions or by air-blowing.

Objections to this method fairly crowd on one another. Vanadium recovery in the mixer would probably be little better than in the ladle or reaction box method as it probably would be difficult to oxidize very effectively. Even granting that the vanadium recovery might be better, owing to the larger

(Oxidation in Open Hearth and Mixer, cont'd) --

reaction surfaces involved, the method would still be difficult to operate as it would involve much additional equipment in the mixer room and carefully controlled circulation of materials. The paramount objection, however, is that the vanadium slag from the open hearth furnace would probably be high in phosphorus and the recirculation of phosphorus in the blast furnace would aggravate the already difficult phosphorus problem of the company. Suppression of phosphorus by early silica additions to the open hearth may be possible, but this would lower the grade of the slag and also probably result in severe attack of the basic lining of the open hearth. In any event, the final vanadium product obtained would probably be high in phosphorus and consequently present a difficult purification problem.

C. Oxidation in New Mixer -

The A or B furnace of No. 2 Shop could be relined acid and used as a 500-ton mixer. All iron could be circulated through this mixer and by running the iron through a highly oxidizing slag, a fair amount of silicon and vanadium could be removed from the iron. If reaction calculations indicate that preferential oxidation of vanadium can be secured at high temperatures (which seems unlikely, as vanadium will probably function in the same manner as does phosphorus which oxidizes better at low temperatures), the desirable reaction can be furthered by supplying heat to the mixer. The heating would also increase the $SiO_2:FeO$ equilibrium ratio in the slag and consequently improve the grade. The main objection to this procedure is that it would necessitate the loss of a badly needed open hearth furnace. There is also danger of sulphur

(Oxidation in New Mixer, cont'd) -

pickup from the high-sulphur flame through the acid slag. According to report the sulphur build-up did not occur when this procedure was followed during a period in 1914 when the company was desiliconizing in a mixer, but sulphur build-up did occur when the iron was desiliconized by partial blowing in a converter and then dephosphorizing in a mixer. The probability is, then, that if a good recovery of vanadium is to be obtained by this method it will involve sulphur build-up in the steel. This would, of course, rule the method out. If, however, this build-up would not occur, the method might be practical as the loss of an open hearth might be more than compensated for by the increase in production of other open hearth units which would occur as a result of the lowering of the silicon content of the iron. In view of the company's previous experience with this method, and considering the possibility that it might involve a drop in steel production, it would probably be difficult to obtain support for this method of vanadium recovery.

D. Use of Basic Converter -

As mentioned in Part I, high-silicon pig containing less than 2 per cent phosphorus cannot be so satisfactorily treated in the basic bessemer converter as the silica produced in the oxidation of the silicon must be neutralized by heavy lime additions and the phosphorus (required as a fuel in the process) is too low. It is not surprising, then, that the company's experience with this method of steel manufacture was not too good and it would not, consequently, seem to be a suitable method of recovering vanadium from the pig. Such a unit could, of course, be operated so that practically only silicon and vanadium are oxidized. The resultant slag, however,

(Use of Basic Converter, cont'd) -

would be high in phosphorus, which would involve purification difficulties.

E. Use of Acid Converter -

If an acid converter were operated so as to oxidize only silicon and vanadium it should be possible to concentrate practically all of the vanadium in the converter slag with little interference with present steel-making procedure. Leaving economics and equipment requirements out of consideration, this would certainly seem to be the best method for recovering the vanadium, for the slag obtained should be fairly low in phosphorus and the recovery should be good. The concentration of vanadium in the slag would be as high as the silicon-vanadium ratio in the pig would allow. This concentration could be increased by recirculating the slag through the blast furnace. The objection to this method is, of course, that it would take a fairly long time to build the necessary equipment and the cost for the reduction of vanadium and silicon would be quite high. The lower silicon iron produced, however, is more suited to open hearth operation than is the high silicon iron being produced at the present time. In view of their previous experience with converters, however, it is doubtful whether the company would be interested in this method of treatment.

PART IV. - SUMMARY AND CONCLUSIONS.

Wabana iron ore smelted by Dominion Steel and Coal contains 0.05 per cent vanadium and 0.95 per cent phosphorus. Practically all of the vanadium and phosphorus is reduced to pig iron in the blast furnace, which uses a coke containing 1.80 per cent sulphur. Blast furnace and open hearth procedures are discussed in Part I of this report. Part II reviews the vanadium recovery experiments made to date, while Part III reviews and analyses the possibilities of various recovery methods.

The following possible methods of vanadium recovery are available:

- A. Oxidation of the vanadium in the pig iron by adding an oxidizing agent to the blast furnace ladle or by oxidizing, prior to open hearth treatment, in a reaction box.
- B. Oxidation of vanadium in a mixer.
- C. Oxidation of vanadium in the open hearth furnace.
- D. Oxidation of vanadium in a basic bessemer unit.
- E. Oxidation of vanadium in an acid bessemer unit.

The low manganese content of the iron is an advantage, as it makes easier the oxidation of vanadium.

The high silicon in the pig iron, however, makes recovery more difficult as a substantial amount of silicon must be oxidized before a good vanadium recovery can be effected. Fluctuations in ore composition and furnace design, however, prevent the regular production of a low silicon iron (see Part I, pages 3-4). There is a possibility that the silicon content of the iron could be reduced should steam be introduced with the blast. This practice, while open to certain objections (see Part I, page 4), has been used successfully before at

(Part IV, Summary and Conclusions, cont'd) -

Sydney. Certainly, the regular production of low silicon iron would greatly facilitate vanadium recovery; so it would seem that consideration might be given to the reintroduction of this procedure.

Solution B would probably not be satisfactory, as there is a danger that sulphur build-up in the iron will occur as the result of the action of the high sulphur products of combustion through the acid slag. Furthermore, the present mixer is not supplied with good handling facilities and the conversion of one of the large basic open hearths to an acid mixer would involve the loss of a large open hearth furnace and a consequent loss in badly needed steel making capacity, although this may be compensated for by the fact that the remaining open hearth furnaces should operate more efficiently on the lower silicon iron.

Solution C is open to the objection that vanadium-containing slag produced in early oxidation in the open hearth would probably be so low in grade that recirculation through the blast furnace would be necessary. If the phosphorus content of the slag should be high, as would probably be the case even if it were kept fairly high in silicon, a practice which would involve attack of the basic furnace lining, the company might not tolerate this recirculation as it would aggravate their already difficult phosphorus problem. (See Part III, page 27). In addition, this method would probably make necessary the treatment of a vanadium product containing a fair amount of phosphorus.

Solution D is none too satisfactory, as the high silicon, intermediate phosphorus pig iron is not very well suited to the basic bessemer process (see Part III, page 28).

(Part IV, Summary and Conclusions, cont'd) -

Solution E, that used by Bethlehem in their treatment of Tofo ore, would probably be satisfactory. However, if present steel making practice must not be disturbed it would be necessary to stop the blow immediately after the silicon and vanadium have been oxidized. Equipment required for this operation would be expensive and would require the best part of a year to build. In addition, the company is definitely prejudiced against a converter installation because their previous experience with this method of treatment was not good. The converter method, however, should work and should allow for a good vanadium recovery (Part III, page 29).

Solution A appears to be the best in view of the necessity of obtaining vanadium immediately with as little interference as possible with steel making operations. It should be possible to obtain an overall vanadium recovery of at least 25 per cent by this method (based on 32 per cent recovery in slag and 30 per cent recovery in the leach) and this recovery could probably be raised if the oxidation were done in a reaction box, if a combined air blowing - scale addition method were used, or if the silicon content of the pig were lowered by introducing steam with the blast.

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