

II.—*On the occurrence of Vanadium in Pig-iron smelted from the Wiltshire Oolitic Iron-ore.*

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SOME time since samples of pig-iron were submitted to me from two different iron-works in Wiltshire, viz., the Seend and the Westbury. Silicium, sulphur, and phosphorus were the only ingredients whose percentages were required to be determined. To estimate these, the usual methods of analysis were employed, viz., oxidising the pig, in small fragments, with fuming nitric acid, adding occasionally a little concentrated hydrochloric acid. The solution was then evaporated to dryness, and heated; the mass then redissolved in strong hydrochloric acid, and the silica separated, the sulphur and phosphorus being determined as described in the Journal of the Society, vol. xvi., page 390 and 391. The following results were obtained :—

The samples of pig examined were all grey, and numbered from No. 1, best foundry, to No. 3; No. 4, best forge, to No. 6 pig, from Seend works.

TABLE I.

No.	Grains of pig taken.	Silica obtained.	Residue by HFl and SO_4H .	$\text{BaO}.\text{SO}_3$.	$2\text{MgO}.\text{PO}_5$.
1	63.14	6.38	.05	.165	1.94
2	63.72	5.03	.08	.360	2.070
3	61.94	4.315	.09	.435	2.125
4	62.41	4.34	.075	.895	1.600
5	62.62	3.11	.085	.730	2.055
6	60.38	2.87	.050	1.095	1.920

Analyses 5 and 6 repeated.

TABLE IA.

A5	23.82	1.335	.16	.215	.74
B6	27.515	1.525	.175	.46	.87

In analyses A5, B6, the oxide of iron was dissolved in the dish in which the first solution of the pig had been evaporated to dryness. The separation of the iron from the silica was not so complete as in the other analyses, when the oxide of iron was detached from the dish and transferred into a beaker in which the oxide was boiled for several hours, the beaker being well covered with a large watch glass. This process is always necessary to separate oxide of iron from silica, and to obtain the silica nearly white after burning. Two samples, No. 1 and No. 5 pig-iron, were from the Westbury Iron Works.

TABLE II.

Number.	Grains of pig taken.	Silica obtained.	Residue by HFl & SO_4H	$\text{BaO}.\text{SO}_3$	$2\text{MgO}.\text{PO}_5$
5	61.28	4.23	.43	.20	3.92
5	62.39	3.545	.275	.37	4.095

TABLE III.

*Results: Silicium, Sulphur, and Phosphorus per cent.**Wiltshire Pig Iron (Grey) from Seend.*

No.	Silicium.	Sulphur.	Phosphorus.	
1.	4.717	.036	.867	} Foundry Pig.
2.	3.659	.077	.917	
3.	3.909	.096	.968	
4.	3.140	.196	.724	} Forge Pig
5.	2.257	.160	.926	
6.	2.197	.248	.898	

Table IV.

Wiltshire Pig Iron (Grey) from Westbury.

No.	Silicium.	Sulphur.	Phosphorus.
1.	3.21	.044	1.806 Foundry.
5.	2.67	.081	1.853 Forge.

It will be seen that the residues from the silica in Table I. are very much less than those in Table II. In Table I. the small amount of residue was chiefly phosphate of iron, due to the oxidation of a small amount of phosphide of iron, which is universally left undissolved by the acid, together with the silica. The residues in Table II. were nearly white; they were fused with bisulphate of potash; complete solution took place. On dissolving, however, in cold water, a gelatinous precipitate was left; this was filtered off, and the clear solution on boiling gave a precipitate, which was at the time considered to be titanous acid.

In preparing my recent paper referred to above, the pig used in Table II. was again examined: it was soon found, however, that the residue from the silica was not titanous acid, although in the interim between my first and second examination, samples of this pig were examined by a friend of mine, and by one of my pupils, both of whom found titanium in the pig, evidently mistaking vanadium for titanium, as will presently be shown.

The method found to be the most advantageous in separating the vanadium from the pig, was the same as that employed to separate titanium, viz., by dissolving the borings in dilute hydrochloric acid, and after the pig was nearly all dissolved, adding some strong acid, and boiling well; the chloride of iron was then filtered off from the graphite and silica, the filter well washed from chloride of iron, and treated with a dilute solution of potash to dissolve the silica; the potash thoroughly washed out; and the filter treated with hydrochloric acid, washed until all the acid was removed, then dried, ignited, and burnt over a Bunsen's burner, or better in a muffle. The residue left was a semi-fused mass, apparently consisting of a mixture of a fusible and infusible oxide, staining a porcelain crucible yellow, and adhering strongly to it, some portions of the mass being of a purplish blue colour, similar to the bloom on a plum.

The following are the residues obtained from different samples

of pig from the two above mentioned localities. It will, however, be seen that the pig from Seend contains less than half that contained in the Westbury pig.

TABLE V.

Westbury Pig Iron (1860) (Grey), No. 1, best Foundry.

	Grains taken.	Gave residue.	Residue per cent.
A.	127·325	·99	·777
B.	1066·72	8·60	·866
C.	246·81	2·19	·887

Sample C was dissolved in dilute commercial sulphuric acid; the residue contained a little iron.

Westbury Pig (Grey), No. 5 Forge Pig.

	Grains taken.	Gave residue.	Residue per cent.
C'.	236·11	2·04	·864

Westbury Pig, 1863, No. 1, best Foundry.

	Grains taken.	Gave residue.	Residue per cent.
D.	231·25	2·088	·901
E.	230·455	1·935	·839

Westbury White Pig, 1863.

Grains taken.	Gave residue.	
231·655	8·200	Residue contained a large quantity of oxide of iron.
134·81	3·435	

Seend Pig, No. 1, best Foundry, 1860.

Grains taken.	gave residue.	Residue per cent.
518·4	1·82	·351

The semi-fused residue treated with concentrated hydrochloric acid, gave off chlorine, and formed a brownish-yellow solution, which, on boiling, soon became of a beautiful green colour, some amount of a black insoluble residue remaining undissolved in the form of a fine powder. On adding nitric acid, no perceptible change took place, and the heavy black residue did not appear to

be at all affected by it. The residue was separated from the black insoluble matter, the soluble portion was evaporated on the water-bath, and the greater part of the free acid evaporated: a syrupy, dark-greenish mass was then left, the sides of the dish being of a brownish colour. On adding water to this, a beautiful blue solution was formed, and a small amount of a white, insoluble, flocculent matter was observed. The solution was green when acid, but blue when free from much excess of acid, or largely diluted with water. On testing this solution, it gave all the characteristic reactions of vanadium-salts, the most marked being the yellow precipitate with ferrocyanide of potassium, which, on standing, acquires a greenish tinge. From the above reaction no iron can be present in the residue. It may be stated that, in the examination of several samples of pig, the graphite has been obtained nearly pure, or mixed with some of the rarer metals occasionally occurring in pig-iron, the oxides of which may be obtained on burning the graphite. For the description of a residue of nearly pure titanitic acid in pig-iron, see the Society's Journal before alluded to, vol. xvi, Table I, page 392.

Examination of the Black Insoluble Matter.—On fusing the substance with bisulphate of potash, complete solution took place; the fused mass, after cooling, dissolved completely in cold water. The solution, heated to the boiling point, gave an immediate precipitate, which settled down as a dense yellowish-white powder. This precipitate was partially soluble in hydrochloric acid, or, if hydrochloric acid were added before boiling the solution, no precipitation took place, thus showing that it was not titanitic acid. The solution, before boiling, gave the distinct yellow coloration with yellow prussiate of potash peculiar to vanadium salts, although a distinct precipitate was not formed until the solution had stood some time.

This black powder is, most probably, suboxide of vanadium; it does not appear to be oxidised, certainly not to any extent, by fuming nitric acid, and appears to be indifferent to acids generally. The precipitate formed on boiling the solution in bisulphate of potash, is a basic sulphate of vanadium. In the various residues obtained from the different samples of pig, the amount of this black residue appeared to be always about in the same quantity. Two determinations were made of the relative quantity of the black oxide, and the results bear out the above conclusion. A portion of residue B (see Table) was weighed out.

Residue B, 3·49 grains, gave black oxide	1·99
Residue E, 2·085 grains, gave black oxide.	1·105

By proportion 3·49 : 1·99 :: 2·085 : 1·19

The results approximate very closely. It would appear that the amount of residue in the various samples of the same pig, made at different times, is the same in amount, and also in composition. This will be seen on examining Table 5. A and B may be taken as identical in the same pig C, containing a little iron. C', quite a different quality of pig, made about the same time as the previous sample, agrees in percentage of residue very closely; D is a trifle higher, and E about the same. It must, however, be observed, that in treating the residue from the pig, insoluble in acids, a second time with hydrochloric acid, after having removed the silica by potash, the acid acquires a darkish brown colour; and if the iron it contains be separated by caustic potash, and the filtrate from the iron be acidified with acetic acid, a distinct yellow coloration is obtained with yellow prussiate of potash, thus showing that a small amount of vanadium is dissolved. In experiment E, the substance was treated twice with potash and hydrochloric acid; this may account for the result being a little lower than D. It was also observed, that if, on dissolving the pig in acid, the clear chloride of iron be poured off, and the insoluble portion boiled for a long time with strong hydrochloric acid, this second portion, on filtering, gave a filtrate which differed in colour from the bright green of protochloride of iron, and was tinged brown; this is most probably due to the solution of a little vanadium. As this pig (Westbury) contained so high a percentage of phosphorus, it was thought advisable to test the residue for phosphoric acid. A determination of this acid was made in residue E. The portion soluble in hydrochloric acid was mixed with chloride of ammonium, tartaric acid, ammonia, and chloride of magnesium, and the solution allowed to stand two days. The ammonia-phosphate separated, dried, ignited, and weighed, gave of pyrophosphate of magnesia ·265, corresponding to ·17 PO₅; the filtrate from the ammonia-phosphate, gave no indications of the presence of iron with yellow prussiate of potash, or with sulphide of ammonium.

The total residue 2·085 diminished by ·17 PO₅ leaves 1·915; hence, assuming that the portion of this residue soluble in acids is

vanadic acid, VO_3 , and that the black residue is suboxide YO , we find for the quantity of vanadic acid,

$$\begin{array}{r} \text{VO.} \quad \text{VO}_3. \\ 1.915 - 1.105 = .81 \end{array}$$

Consequently, the equivalent of vanadium being 68.6, the percentage of metal will be—

$$\begin{array}{rcccl} \text{VO.} & \text{V.} & \text{VO.} & \text{V.} & \\ 76.6 : 68.6 & :: 1.105 : .989 & & & \\ \text{VO}_3. & & \text{VO}_3. & & \\ 92.6 : 68.6 & :: .81 : .60 & & & \\ \text{Pig.} & \text{V.} & & \text{V.} & \\ 231.25 : 1.589 & :: 100 : .686. & & & \end{array} \left. \vphantom{\begin{array}{rcccl} \text{VO.} & \text{V.} & \text{VO.} & \text{V.} & \\ 76.6 : 68.6 & :: 1.105 : .989 & & & \\ \text{VO}_3. & & \text{VO}_3. & & \\ 92.6 : 68.6 & :: .81 : .60 & & & \\ \text{Pig.} & \text{V.} & & \text{V.} & \\ 231.25 : 1.589 & :: 100 : .686. & & & \end{array}} \right\} = 1.589.$$

Two trials were made to endeavour to obtain vanadium from white pig; it was, however, found impossible to separate the iron completely. As in the case of the other pig, the residue obtained in the first experiment was treated similarly to the grey pig; in the second, the residue, after dissolving out the iron in dilute acid, was boiled with concentrated acid for some time, and after filtering off the insoluble matter, was treated twice with potash and hydrochloric acid alternately, to see if the iron could not be dissolved out; it was, however, as is seen by the result, unsatisfactory; had it been possible to separate the vanadium from the white pig, it would have been far more advantageous, as the grey pig leaves a considerable amount of graphite, which requires much time to burn.

2lbs. of the pulverised pig were operated on with dilute sulphuric acid, the silica being dissolved with potash; the residue obtained by burning the graphite contains, however, some amount of iron. A little vanadic acid was prepared from this by treating the pulverised residue with ammonia, allowing it to stand some time, then gently warming it: the ammoniacal solution was of a deep red colour; this, when evaporated and allowed to stand, deposited a considerable amount of oxide of iron, and small distinct granular crystals attached themselves to the beaker. The solution filtered from oxide of iron was colourless; on evaporating it to dryness and heating it, the vanadic acid separated, first of a beautiful orange-red colour, then green; and on heating more strongly, it assumed a dirty greyish green colour. If the residue when free from iron is treated with ammonia, a beautiful yellow solution is obtained,

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which, if it has been heated, deposits, on cooling, small granular crystals of vanadate of ammonia. The residue from the 2lbs. of pig, after being treated with ammonia, was dissolved in hydrochloric acid, the liquid being boiled for many hours; it was then filtered from the greyish residue, and the solution evaporated, to expel the larger portion of free acid. It then deposited on the sides of the beaker a white, amorphous, light substance, which adhered strongly to the glass. This has not yet been examined; it appears to be insoluble in hydrochloric acid. Nitric acid was added to expel the hydrochloric, the larger portion of the free acid driven off, and the solution then treated with ammonia, which threw down an abundant precipitate of oxide of iron. The filtrate, however, contained only a trace of vanadic acid, the whole being precipitated by the ammonia with the iron.

The ore has not yet been tested for vanadium. The following is the analysis of the Seend ores, made by me some time since:—

Seend Iron Ore.				Metallic Iron.	
Silica	18.02		
Peroxide of iron	64.61		
Alumina	3.85		
Lime64		
Magnesia20	45.22	
Phosphoric acid64		
Combined water	10.21		
Moisture	1.64		
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99.81					

An account of the analyses of the Westbury ore will be found in the Journal of the Society, vol. xv, page 334. Some remarks are made respecting the oxide of iron obtained, the weight of which could not be made to correspond with the results obtained by standard solution. Now that vanadium has been found in the pig, it is most probable that some vanadic acid is contained in the oxide of iron; the author proposes, however, to re-examine the ore, and lay the result before the Society at some future time. This pig iron will readily furnish any quantity of the hitherto somewhat rare metal vanadium, with tolerable facility. Vanadium is, however, now obtained as a waste product from bauxite, in the manufacture of aluminium, to what extent the author cannot say, or whether it would be a better source for the metal than the pig-iron.

This pig-iron appears to contain more vanadium than that made from the Taberg ore, in Sweden; and, so far as the author is aware, it affords the first instance in which this metal has been found in English pig-iron; some mention is made of its occurrence in a Staffordshire slag (Chem. Gaz. 1848, page 298), by Dick, but only a mere notice is given of it.

At the present time, a large quantity of the pig, about 17lbs. is being dissolved in acid, and in a short time the author hopes to lay some further results before the Society, as to the state in which the vanadium occurs in the ore, and the influence it has upon the iron.
