XLVI.—*On the Occurrence of Titanium in Pig-iron, and some Remarks on the use of Titaniferous Minerals in the Manufacture of Iron and Steel.*

By EDWARD RILEY, F.C.S.

[Read at the Newcastle Meeting of the British Association.]

THE presence of small cubical red crystals, with a metallic lustre, has long been observed in the hearths of old blast-furnaces—they may be said, in fact, to be universally present to a greater or less extent—occurring most largely in the hearths of furnaces where clay ironstone, or silicious iron ores (such as the red hematite and Forest of Dean ores) are used. The crystals are always more abundant when the furnaces are used for making the best grey iron, the most perfect crystals that have come under my observation being some from the Low Moor ironworks; while the largest quantity were from the ironworks in the Forest of Dean, and the Pontypool ironworks, some of which crystals were massed together, and had the appearance of copper. The iron from the above works has a great commercial reputation for its quality, and as a rule, the better the quality of iron made in a blast-furnace, the greater is the quantity of titanium found in the hearths.

The examination of a large number of the hearths of the Welsh blast-furnaces, where common iron for rails and bars is chiefly made—in one works eighteen were inspected during their removal—the crystals were observed disseminated through the mass, but were only very small in size and minute in quantity.

The red crystals were first supposed by Wollaston to be titanium; but Wöhler subsequently showed them to be a mixture of nitride and cyanide of titanium, containing 18 per cent. of nitrogen and 4 per cent. of carbon. The composition of the crystals, however, varies—as some will be found to be readily converted into titanous acid on boiling with strong nitric acid, whereas others are quite unattacked by this re-agent.

Until recently the source of these crystals had not been very

clearly accounted for, as in all analyses of materials used in the blast-furnace, titanitic acid or the oxide of titanium was very rarely if ever mentioned. Titanitic acid has hitherto been considered an oxide occurring only in minute quantity, or found in minerals that are not largely disseminated—such as in Rutile and Anatase, in the pure or nearly pure state, in Iserine, Ilmenite, and numerous other minerals mostly mixed with a large percentage of iron. The following are two analyses of some Norwegian ore that has been used in the blast-furnace, and will be subsequently referred to:—

	1.	2.
Magnetic oxide of iron	46·14*	54·72
Titanic acid	36·88	40·80
Silica	13·32	1·58
Magnesia	2·07	2·13
Lime	·78	·66
Bisulphide of iron (iron pyrites) ..	1·05	—
	<hr/> 100·24	<hr/> 99·89
Metallic iron	<hr/> 33·39	<hr/> 39·62

No phosphoric acid was detected.

An experience of eleven years, in the almost exclusive examination of ores and products from iron works, has proved to me that titanium ought no longer to be considered one of the rarer elements, as it occurs very generally disseminated, and is a universal constituent of all clays, as was pointed out by me in a paper read before the Chemical Society last year, whence it seems that in furnaces where clay ironstone is used, the source of the titanium is the clay in the ore and the shale attached to it. In silicious ores, such as the hematites, the titanium is most probably obtained from Rutile, which is frequently found in quartz, and perhaps partly from the fire-bricks, and from the shale which is frequently used.

The minerals of titanium, viz., Rutile, and Titanic acid mixed with iron, are largely found in Norway, and can be brought over to this country at a very cheap rate. Rutile, which, commercially speaking, is pure titanitic acid, can be purchased here for 10*l.* per ton, or even less if it were taken in large quantity; and iron ores, such as shown in the analyses given, can be bought at from 20*s.* to 40*s.* per ton.

Recently a series of patents has been secured by Mr. R. Mushet, for the use and application of titanium in the manufacture of iron and steel, and for alloying titanium with iron and

* These analyses were made in my laboratory by my late pupil, Mr. Betley.

steel, in which very beneficial results are claimed for the action of the titanium.

Before entering upon the question as to the effects of titanium, it will be well to consider if titanium alloys with iron, and, if so, to what extent. Up to the end of 1862 I had examined many samples of pig-iron, and Mr. Mushet's steel itself specially, with the view of detecting titanium; but in no case could I obtain any distinct evidence of its presence, except occasionally as a minute trace. My conclusion at that time was that titanium did not alloy with iron, and my opinion on this point was strengthened by the results of M. St. Claire Deville, of Paris, who has paid especial attention to the subject; Dr. Percy has also observed that he could never find it. M. Deville mentioned to me, in the course of some conversation on the subject, that he had occasionally seen red crystals of titanium in the pig itself, and it was only then that he could detect the presence of the metal. The general opinion of English chemists, who had paid attention to the subject, was that titanium did not practically alloy with iron.

At the end of last year some samples of pig-iron were submitted to me, one of which was made from red hematite mixed with $7\frac{1}{2}$ per cent. of Norwegian ore, similar to that of which the analyses have just been given. The analysis of this sample of pig gave distinct evidence of the presence of an appreciable amount of titanium; and in other samples, sent at the same time, reported to be made from red hematite alone, to my surprise titanium was also found, but not quite to such a large amount. This could not be satisfactorily accounted for until the persons sending me the pig, informed me that 10 per cent. of Irish (Belfast) ore had been mixed with the hematite; and on examining this ore, it was found to contain some amount of titanium, as seen by the following analysis:—

BELFAST IRON ORE, dried at 280° Fahrenheit.

Silica	9.87
Peroxide of iron	27.93
Protoxide of iron	5.08
Alumina	34.57
Titanic acid	3.51
Manganese	traces
Lime	.91
Magnesia	.62
Combined water	19.36
Phosphoric acid and copper	traces
	<hr/>
	101.85
	<hr/>
Metallic iron %	23.5

The use of this ore in the furnace was attended with considerable advantage, on account of its high percentage of alumina, thus forming a more readily fusible double silicate with the silica contained in the hematite.

The method pursued to detect titanium was the same as that adopted and given in my paper in the Journal of the Chemical Society for 1862, page 311. It however required no very special method to point out its presence, and it was readily found in the silica obtained in the portion of pig used for the determination of phosphoric acid, by simply treating the silica with hydrofluoric and sulphuric acids, evaporating to dryness and igniting. Thus 120·845 grns. of pig gave silica 4·29, which left a residue, when treated as above, of 0·31. This was slightly tinged in colour by iron, and on fusing it with bisulphate of potash, dissolving the fused mass in cold water, and boiling, the characteristic precipitate of titanate of iron was obtained, which gave the reactions peculiar to titanate of iron in the blowpipe flame with microcosmic salt. The whole of the titanate of iron cannot be separated with the silica, and a considerable amount is in solution with the iron.* However, to

* The following are methods which have been adopted to separate the titanate of iron :—A weighed portion of the borings of the pig are treated with fuming nitric acid in a flask, a few drops of hydrochloric acid added from time to time, the whole being well boiled. The contents of the flask are then transferred into a porcelain dish, evaporated to dryness and heated strongly. On cooling, it will be found that oxide of iron readily detaches itself from the dish, and can be easily transferred into a beaker, the portions left on the dish being dissolved in hydrochloric acid, and poured on the contents of the beaker; the dish may be washed, or nearly so, with strong hydrochloric acid. The contents of the beaker are boiled for two or three hours until complete solution of the iron is effected; and as some quantity of hydrochloric acid is required for this, my usual plan is to allow a large portion of the excess of acid to evaporate in the beaker, retaining only as much as is requisite to keep the iron in solution. The silica is filtered off in the usual way, after diluting with water and adding a few drops of hydrochloric acid on the filter to dissolve the basic salt formed by the water. By this means the silica can be obtained very nearly white after burning off the graphite, and very little iron will be found with it, unless the pig contains much phosphorus, as the silica invariably contains more or less phosphate of iron from insoluble phosphide of iron, which cannot be completely dissolved out by hydrochloric acid. In the filtrate from the silica the sulphur in the pig may be determined, and subsequently the phosphoric acid, by first removing the excess of chloride of barium used to precipitate the sulphuric acid. Before determining the titanium and phosphoric acid, the residue from the silica should be fused with bisulphate of potash, dissolved in water, and added to the solution of iron in which the phosphorus and titanium are to be determined. The solution is reduced with sulphite of soda, and the excess of sulphurous acid driven off by boiling. The solution is then nearly neutralised with ammonia, and acetate of ammonia or soda added; and if there is only a small quantity of phosphoric acid,

determine accurately titanic acid, oxide of iron ought to be entirely absent, as it either prevents its precipitation altogether, or materially retards it. This is in fact the great reason why titanic acid has been so frequently overlooked, and so many errors made.

Titanium may, however, be found more satisfactorily and more readily, during the process usually adopted to determine the amount of graphite in pig-iron, provided a large quantity of the pig be operated on. In the analysis of the pigs alluded to, about 200 grains of the pig were dissolved in dilute hydrochloric acid; when the pig was nearly all dissolved, and the action of the acid had ceased, more hydrochloric acid was added, and the solution well boiled, so as thoroughly to extract the iron. The solution was then thrown on dried counterpoised filters encircling each other, and the filter well washed to remove all the iron. It was then treated with dilute potash, and washed once; then re-treated with it, so as entirely to remove the silica. The potash

there will always be sufficient peroxide of iron to precipitate it, but if not, a few drops of nitric acid must be added, so that the precipitate produced is distinctly red, and the solution is boiled and filtered as quickly as possible. This precipitate may be at once treated, or if it contains much peroxide of iron in excess of that sufficient to form phosphate of iron, it is better to re-dissolve it in hydrochloric acid, re-reduce it with sulphite of soda, and repeat the operation above described. The precipitate is then dissolved in hydrochloric acid, and chloride of magnesium, ammonia, chloride of ammonium, and tartaric acid added, the precipitate produced being allowed to stand two nights; then the ammonia-phosphate of magnesia is filtered off, dried, ignited, and weighed, and the phosphoric acid calculated from the pyrophosphate of magnesia. The filtrate from the phosphoric acid is treated with sulphide of ammonium, and the sulphide of iron separated, the filtrate evaporated to dryness, ignited, and burnt in a muffle; or evaporated nearly to dryness, transferred into a Florence oil-flask, and treated with fuming nitric acid until all the tartaric acid is destroyed; in either case the residue is fused with bisulphate of potash, or where nitric acid is used, this is driven off with sulphuric acid. The product of the fusion with bisulphate of potash is dissolved in cold water, boiled for some hours, and allowed to stand a night in a warm place, when the titanic acid is filtered off and washed with dilute sulphuric acid—dried, ignited, and weighed. If the determination of phosphoric acid is not required, then the precipitate produced (either by one treatment or two) by the alkaline acetate, may be dried (without washing), burnt, and fused with bisulphate of potash, and dissolved in cold water, when a little phosphate of iron, which remains insoluble, is separated; and the solution being boiled, the titanic acid is precipitated, and may be separated as before.

Neither of the above two processes is very satisfactory for the quantitative determination of titanic acid. The first is very tedious, and the destruction of the tartaric acid very troublesome; while in the second method, the phosphate of iron (insoluble in the bisulphate of potash) cannot be washed without passing through the filter; very frequently also the small amount of iron keeps up the titanic acid, as iron, even in small quantities, has a very great effect in preventing the precipitation of titanic acid, so that it is always advisable to add a little sulphite of soda, which reduces the oxide of iron and facilitates the precipitation of the titanic acid.

was thoroughly washed out and the filter treated with hydrochloric acid, thoroughly washed, and dried at 250° Fahrenheit, until the weight was constant. This gave the graphite, on burning which, a residue of a dirty light brown colour was left, which, on being fused with bisulphate of potash and treated as before, proved to be nearly pure titanitic acid, as will be seen from the results below :—

		Grains of Pig taken.	Graphite and Titanic Acid.	Residue after Burning.	Titanic Acid obtained.
No. 1 Pig	..	205·68	7·82	1·23	1·085
„ 2 „ ..	..	207·05	7·85	·835	·745
„ 3 „ ..	..	216·86	7·04	·33	·28

The amount of titanitic acid, or rather residue, obtained from the silica after it had been volatilised with hydrofluoric and sulphuric acids, when the pig was dissolved in nitro-hydrochloric acid, evaporated to dryness, and re-dissolved in hydrochloric acid—is given below :—

		Grains of Pig taken.	Silica obtained.	Residue by Hydrofluoric and Sul- phuric Acids.
No. 1		120·845	4·29	·31
„ 2		127·93	8·659	·20
„ 3		122·55	9·22	·265

This residue, chiefly titanitic acid, contained, however, some iron, and was not so pure as that obtained by burning the graphite, given in the above table. The following are the tabulated results of the analyses of the three samples of pig :—

		1.	2.	3.
Carbon..		3·31	3·18	3·11
Silicium		1·86	3·28	3·55
Iron ..		93·47	92·79	92·04
Manganese		·50	·48	1·09
Sulphur		·071	·058	·112
Phosphorus		·076	·062	·093
Titanium		1·150	·71	·470
		<u>100·437</u>	<u>100·560</u>	<u>100·465</u>

In all these the carbon was combined; and traces of antimony, nickel, copper, and cobalt were found in all three samples.—Samples 1 and 2 were No. 3 grey iron; and sample 3 was bright iron.

The percentage of titanium given in the above analyses differs from that in the preceding table, probably in consequence of the hydrochloric acid dissolving some of the titanium. From 15 to 16 grns. of the pig are dissolved in nitrohydrochloric acid, and the solution evaporated to dryness; the silica separated in the usual way and volatilised with hydrofluoric and sulphuric acids; the residue fused with a little bisulphate of potash, dissolved in cold water; and the liquid added to the filtrate from the silica. The solution is precipitated with acetate of soda or ammonia, first nearly neutralising it with ammonia; after boiling well, the basic peracetate of iron is filtered off, and well washed, adding occasionally a drop or two of the alkaline acetate. The filter is then dissolved in hydrochloric acid, and peroxide of iron precipitated by ammonia, filtered, dried, and ignited in the usual way. The peroxide of iron is then dissolved in hydrochloric acid, and the small amount of silica present separated; the solution is reduced with sulphite of soda; and the iron determined with a standard solution of bichromate of potash. This gives the percentage of iron, or of pure peroxide of iron; and the difference between the peroxide of iron weighed, and that determined by standard solution, is considered to be titanous acid and phosphoric acid. The phosphoric acid having been determined by another distinct operation, the amount present in the peroxide of iron is calculated and deducted from the above difference—the remainder being considered to be titanous acid, from which the percentage of titanium in the pig is calculated. This determination by loss is not so satisfactory as a direct determination, and is probably a little high; and the true percentage of titanium will probably lie between that given in the table and that in the analyses. Subsequently to the analyses of the above three samples of pig, a sample of iron made wholly with hematite was tested for titanium, but none was detected. Recently I have examined some samples of pig-iron made from a mixture of Cornish ores, Irish bog-ore, and hematite ore; the result shows that the pig contains some amount of titanium; the following is a partial analysis* of the Cornish ores used:—

Silicious matter	..	..	23·38	21·70	27·18	21·03
Peroxide of iron	..	..	41·96	56·32	47·32	70·20
Peroxide of manganese	..	..	25·77	16·11	16·25	2·45
			—	—	—	—
Percentage of metallic iron	..	..	29·38	39·43	33·14	49·14
„	„	manganese	16·08	10·25	10·34	1·55

These ores contained a little phosphoric acid.

* Analysis made in my laboratory by Mr. Betley.

The following are the results of the analyses of three samples of this pig, the titanium being determined as in the other analyses of pig given :—

	I.	II.	III.
Graphite	3.12	3.010	2.615
Combined carbon.. ..	.310	1.020	.074
Silicium	2.590	2.550	3.325
Iron	87.900	86.880	84.256
Manganese	5.850	6.370	8.087
Nickel and cobalt.. ..	.060	.110	—
Copper with a little antimony ..	.060	.045	.064
Phosphorus	.147	.154	.201
Sulphur	.026	.026	.017
Titanium	.790	1.150	1.629
	<hr/> 100.853 <hr/>	<hr/> 101.315 <hr/>	<hr/> 100.268 <hr/>

Samples I and II were made with a mixture of $\frac{1}{3}$ Cornish ore; $\frac{1}{3}$ Irish bog-ore, $\frac{1}{3}$ hematite; and sample III, $\frac{1}{3}$ Irish bog-ore, $\frac{2}{3}$ Cornish ore. The Irish bog-ore contained 7 to 9 % of manganese.

These samples of pig were Nos. 1 and 2, with here and there patches of bright iron. Nos. 1 and 2 were drilled, but were rather hard; No. 3 was too hard to drill, or could only be drilled with great difficulty. They were made specially to see to what extent, on a large scale, manganese could be made to alloy with iron; and also if a pig could not be made in this country similar to *Spiegeleisen*, and adapted for the purpose of carbonising the iron after blowing by the Bessemer process. The percentage of manganese in the analysis of sample III is the highest that has ever come under my notice in grey pig-iron.

The question now arises—In what state does the titanium exist in the pig—is it, or is it not, alloyed with it? The pig itself has been carefully examined with the microscope to see if any red nitride crystals could be discovered, but no indications of them have been seen. The residue, after dissolving the pig in hydrochloric acid, washing out all soluble matter, and drying, has also been examined, but only distinct graphite plates could be seen, with transparent gelatinous silica, having the appearance of chalcedony; and also some of this residue, after the silica had been separated, was examined, but no indication of any other substance besides the graphite could be seen. From the above it is evident that the titanium must be either disseminated through the pig in a finely divided amorphous condition, or it must be alloyed with it.

Samples of Mr. Mushet's steel, in the manufacture of which titaniferous ores had been used, were also examined, but in no

case was any evidence of the presence of titanium afforded. Several experiments conducted on a small scale with titaniferous iron ores show that no increase in the yield of iron is obtained by the presence of titanitic acid, and that when this substance is present in any quantity it is very difficult to flux, or to get a good cinder; so that it is always necessary to have a large amount of an easily fusible silicate, before satisfactory results can be obtained in the reduction of ores containing titanitic acid. The following are the results of the dry assays of some titaniferous iron ore, containing by wet assay 39·08 per cent. of iron :—

		1.		2.	
Iron ore		500	500	500	500
Clay		100	100	50	100
Lime		250	230	150	180
Anthracite		80	75	75	70
		<hr/>	<hr/>	<hr/>	<hr/>
		930	905	775	850
		<hr/>	<hr/>	<hr/>	<hr/>

The two assays marked 1 were perfect, and a good button of iron obtained, yielding 37·76 per cent. of iron in the ore, the cinder being of a dark blue colour; but in the assays marked 2, the cinder was almost black, semi-fused, and contained cavities with acicular crystals.

It must, however, be admitted, that when titanitic acid is present in iron ores, it appears to impart a steely nature to the iron reduced from them, somewhat similar to that obtained by the use of manganese; and fluxes that have been used with advantage at Sheffield have, on analysis, been proved to contain a high percentage of titanitic acid. The pig-iron made with $7\frac{1}{2}$ per cent. of titaniferous iron ore, of which the analysis is given, proved also to be an iron of very great strength, and excellent quality both for castings and for the Bessemer process.

In conclusion, my opinion as to the use of titanium is, that it appears to have some beneficial effect in the manufacture of iron and steel, and to act somewhat similarly to manganese. The rationale of its action possibly is that the titanium acts as a carrier of cyanogen to the steel, from its known affinity for carbon and nitrogen. The action of manganese is, however, by no means well understood; the same may be said of the cyanides; and to determine it requires the experiments to be more carefully conducted than has been hitherto done, before we can solve the question as to the part (if any) that nitrogen plays in the manu-

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facture of steel. The above points are at the present time engaging my attention; but my object in this paper is to prove that under certain conditions titanium is a constituent part of pig-iron, and not to enter into theoretical considerations on the composition of iron and steel.