

VIII.—*The Chemical Changes which Pig Iron undergoes during its conversion into Wrought Iron.*

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WISHING to make some improvements in the manufacture of iron, we carefully examined the various analyses which had been made of pig and wrought iron, and we found that no comparison could be drawn between the results, as the samples analysed had been obtained from different sources; and also that no detailed analysis had been published of the various chemical changes which pig iron undergoes in puddling during its conversion into wrought iron. We therefore at once decided to undertake this task, with the hope of throwing some light upon this important operation. Fully to investigate the progressive and interesting chemical changes which cast iron undergoes during its conversion into wrought iron, we took samples every five or ten minutes after the pig iron had melted in the furnace. These chemical actions are clearly defined in the furnace by the peculiar appearance which the mass assumes as the operation proceeds. Before describing the various chemical changes, the appearance of the melted mass as taken out of the furnace, and its composition, we shall describe, with some detail, the analytical processes which we have adopted to determine the various elements which exist in pig and wrought iron, and in the samples taken during the puddling.

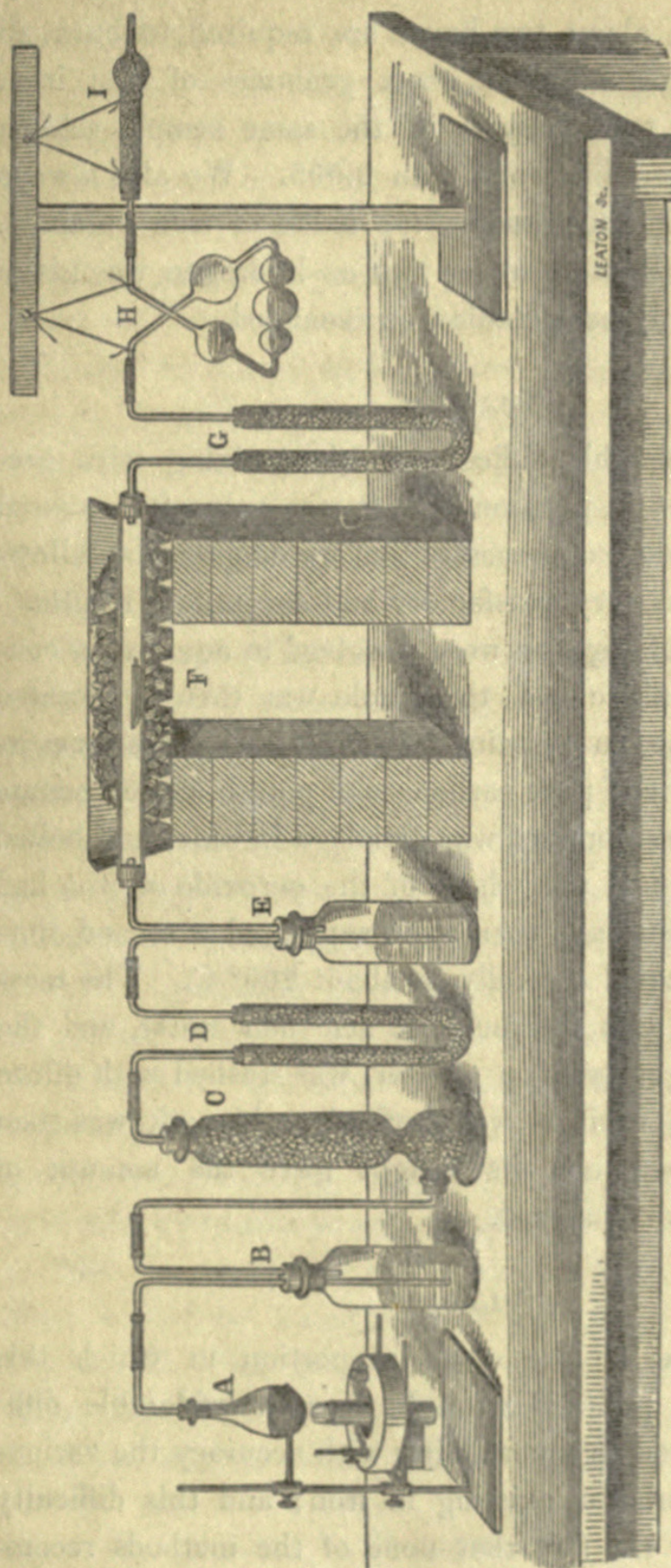
These details of analysis appear to us the more important when it is remembered that most of the heterogeneous substances existing in pig iron, are present only in minute quantities, and that it is on their gradual removal or decrease that the subsequent quality of the wrought iron depends. Also, it is necessary to bear in mind, that we had to trust entirely to the exactitude of the analytical methods adopted to appreciate the chemical changes which gradually took place in the melted mass during the hour and a quarter that the conversion of the cast into wrought iron lasted.

IRON.

The quantity of iron was determined by dissolving one gramme of iron in pure hydrochloric acid, reducing the solution to a perfect protosalt by a little pure zinc, and then determining the amount of iron by Margueritte's process.

CARBON.

To determine this element we found, after many trials, that the best process was to reduce the iron into very fine powder, either by pulverization or by means of a file, and then to burn the carbon under the influence of a red heat by a slow current of pure and dry oxygen gas. The apparatus which we used was the following:—



A. A flask containing a mixture of chlorate of potash and oxide of copper, which by gently heating gave off a regular current of oxygen.

B. A bottle containing a concentrated solution of caustic potash, so as to retain any chlorine or any oxygenated compound of this gas, which might be produced.

C. A tube full of pumicestone moistened with solution of caustic potash, and employed with the same view as the last.

D. A U tube filled with pieces of solid melted caustic potash, also used for the same purpose.

E. A bottle containing sulphuric acid, for retaining any moisture which might accompany the oxygen gas.

F. A porcelain tube in which was placed a small porcelain dish containing the pulverized cast iron.

G. A tube filled with small pieces of pumicestone moistened with sulphuric acid, with the view of retaining any moisture.

H. A Liebig tube full of a concentrated solution of caustic potash, to determine the amount of carbonic acid produced by the combination of the oxygen with the carbon of the cast iron.

I. A small tube with fragments of caustic potash, to retain any trace of carbonic acid which might not be absorbed in the Liebig tube.

To render the absorption of the carbonic acid complete, it is necessary to conduct the operation very regularly and

slowly; therefore, about two hours are required to burn all the carbon existing in about three grammes of cast iron. By this method, two analyses of the same sample seldom presented a greater difference than 0.005. We also always took the precaution to dissolve the oxide of iron obtained, after combustion, in order to see that no hydrogen was given off and consequently no metallic iron remained.

SILICIUM.

There is considerable difficulty in determining with precision this element in pig iron, and it was only after several fruitless trials of various processes that we adopted the following, which gave us very satisfactory and concordant results.

Five grammes of pig iron were dissolved in aqua regia containing excess of nitric acid, the whole was then evaporated to dryness and fused in a platinum crucible with three times its weight of a mixture of pure carbonate of potash and carbonate of soda. The mass obtained was dissolved in water and boiled with aqua regia until the whole of the peroxide of iron had entered into solution, and then was evaporated a second time to dryness and heated carefully to about 200° C. The mass was then heated with hydrochloric acid and water, and the silica, on being gathered on a filter, was washed with dilute hydrochloric acid until it was perfectly white; it was then dried, and calcined, and its weight gave the amount of silicium in the iron analysed.

SULPHUR.

In consequence of the small proportion in which this element exists in pig and wrought iron, considerable difficulty is experienced in ascertaining with accuracy the various proportions of sulphur existing in iron; and this difficulty was increased by the fact that none of the methods recommended gave satisfactory results in our hands. Thus, for example, the method which consists in determining the sul-

phur in the state of sulphuretted hydrogen failed, owing to the difficulty of removing the last traces of sulphuretted hydrogen held in solution in the liquid in which the iron is dissolved and in which the gas is produced. As to the process which consists in dissolving the iron in aqua regia and boiling off the greatest part of the acid and then adding nitrate of baryta to the solution, it cannot be followed with security, for one of us has shown that sulphate of baryta is soluble in acid liquors, especially in those containing nitric acid, and often in such quantities as to make a greater difference between the analyses of two samples of the same iron than the real difference which exists in two samples of iron from different ores.

These considerations induced us to modify the last mentioned process in the following way. Five grammes of the sample of iron to be analysed were reduced to fine powder and gradually and slowly added to a strongly oxydizing aqua regia, composed of four parts of fuming nitric acid and one part of hydrochloric acid. The iron being dissolved, the solution was evaporated to the consistence of a thin syrup, and then gradually mixed with four times its weight of a mixture of pure carbonates of potash and soda, and heated to redness for one hour in a platinum crucible. The fused mass was then heated with boiling water until all the soluble portion was dissolved. This liquor was then rendered slightly acid with hydrochloric acid, evaporated to dryness, and heated at 200° C., to render the silica insoluble. The whole was then heated by water slightly acidulated with acetic acid, and on the silica being separated by filtration, the amount of sulphate, and consequently, of sulphur, was determined, from the weight of sulphate of baryta obtained.

PHOSPHORUS.

We also attached great importance to the exact valuation of this body, because, like sulphur, its presence even in small

quantities is most injurious, the more so as such minute quantities as a few thousandths more or less will completely alter the value of this metal for many uses. To determine phosphorus, the process which we followed was similar to that employed for the sulphur, with this difference, that we added to the liquid from which we had separated the silica, a little hydrochloric acid, and then ammonia in excess, instead of acetic acid, as we had done in the analysis for sulphur. The liquid was allowed to stand to see if any alumina separated, and if not, we added hydrochloric acid in excess, then pure chloride of calcium and then ammonia again, when phosphate of lime, having the following formula $\text{P}_0,3\text{Ca}_0$, was precipitated, from which the quantity of phosphorus was calculated. We always took care to operate on such a bulk of fluid as to prevent the precipitation of any sulphate of lime, and we also washed rapidly to prevent any carbonate of lime being formed. We verified this method several times during our analyses, by determining the amount of lime in our precipitates and the amount of phosphoric acid by M. Reynoso's process.

ALUMINUM.

If there was any alumina it was separated during the last process, and its amount determined.

We also made several fusions of iron dissolved in aqua regia, and evaporated with a mixture of alkaline carbonates to which we had added a little caustic alkali and we found no alumina or mere traces in the iron analysed by us.

MANGANESE.

Five grammes of iron were dissolved in aqua regia, and the whole evaporated to dryness and calcined with alkaline carbonates. The fused mass was treated with boiling water, and to the solution were added small pieces of Swedish paper, to reduce the manganese.

The iron and manganese were then collected on a filter, well washed, and then dissolved in hydrochloric acid. This solution was again evaporated, and heated so as to render the silicic acid insoluble.

The residue was then heated with weak hydrochloric acid, and the solution filtered to separate the silica; carbonate of baryta, recently prepared, was then added to precipitate the oxide of iron; this was separated by filtration, sulphate of soda and a little hydrochloric acid were added to the liquid, to separate the baryta in solution, and finally the manganese was precipitated by a little caustic potash, washed, dried, calcined, and its amount ascertained.

It is necessary that we should describe, in a rapid manner, the physical conditions which pig iron assumes during its conversion. When first melted in a puddling furnace it forms a thick pasty mass, which gradually becomes thin and as fluid as mercury. When it has reached this point it experiences a violent agitation, technically called "the boil," which is produced, no doubt, by the oxidation of the carbon and the escape of the carbonic oxide then generated. During this period of the operation the mass swells to several times its primitive bulk, and the puddler quickly agitates the melted mass to facilitate the oxidation of the carbon. After a short time the mass gradually subsides, the puddler then changes his tool and takes the "puddle" to gather with it the granules of malleable iron floating in the melted mass of scoria or slag. The granules or globules of iron gradually weld together and separate from the scoria, and this separation is hastened by the puddler gradually forming large masses, called balls, weighing from 70 to 80 lbs., from which the scoria drains out.

This part of the operation requires great skill, as nearly the whole of the carbon has been oxidized, so that if the

current of air is not managed with great care the iron itself is oxidized, or, as it is technically termed, "burnt;" and thus not only does great loss ensue in the quantity of malleable iron produced, but also the iron containing a certain quantity of oxide of iron is brittle and of bad quality.

We shall now examine the various chemical changes which pig iron undergoes during its conversion into wrought iron.

The iron we took for our experiments was a good cold blast Staffordshire iron, the pig was rather grey, being of the quality used for making iron wire, or a grey No. 3. Its composition was as follows:—

	First Analysis.	Second Analysis.	Mean.
Carbon	2.320	2.230	2.275
Silicium.....	2.770	2.670	2.720
Phosphorus	0.580	0.710	0.645
Sulphur	0.318	0.288	0.301
Manganese and Aluminum...	Traces
Iron... ..	94.059	94.059	94.059
	<hr/> 100.047	<hr/> 99.957	<hr/> 100.000

FIRST SAMPLE, taken out of the furnace at 12 40 p.m.

Two hundred and twenty-four pounds of the above pig iron were introduced at twelve o'clock, on the 14th of April, 1856, into a puddling furnace, which had been cleaned out with wrought iron scraps. After 30 minutes the pigs began to soften and to be easily crumbled, and 10 minutes more had hardly elapsed when they entered into fusion. A sample was immediately taken out from the centre of the melted mass, with a large iron ladle, and poured on a stone flag to cool. The flue of the furnace, which had hitherto been kept open, was now nearly closed by a damper at the top of the chimney, so that the products of combustion came out by the door of the furnace and other openings, whilst little or none escaped by the chimney.

APPEARANCE OF THE SAMPLE.—On breaking the sample as taken out of the furnace, it had no longer the appearance of grey No. 3 pig iron, but had a white, silvery, metallic fracture, similar to that of refined metal. The rapid cooling of the sample was, no doubt, the cause of the change noticed, for it contained quite as much carbon as the pig iron used; and, further, the carbon was in a very similar condition, as in both cases a large quantity of black flakes of carbon floated in the acid liquors in which the iron was dissolved. The following is the amount of carbon and silicium which the above sample contained per cent.

	First Analysis.	Second Analysis.	Mean.
Carbon	2.673	2.780	2.726
Silicium	0.893	0.938	0.915

These results are highly interesting, as they show that the iron had undergone, during the 40 minutes which it had been in the furnace, two opposite chemical changes; for, whilst the proportion of carbon had increased, the quantity of silicium had rapidly decreased.

This curious fact is still further brought out by the sample which we took out of the furnace at 1 p.m., or 20 minutes later than the last sample analysed, as is shown in this table.

	Carbon.	Silicium.
Pig Iron used	2.275	2.720
First Sample taken out at 12.40	2.726	0.915
Second Sample taken out at 1 p.m.	2.905	0.197

Therefore the carbon had increased 0.630 or 21.5 of its own weight, and the silicium had decreased in the enormous proportion of above 90 per cent. It is probable that these opposite chemical actions are due, in the case of the carbon, to the excess of this element in a state of minute division, or in a nascent state, in the furnace, and that under the influence of the high temperature it combines with the iron, for

which it has a great affinity; whilst the silicium and a small portion of iron are oxidized and combined together to form protosilicate of iron, of which the scoria or slag produced during this first stage of puddling consists, and which plays such an important part in the remaining phenomena of the puddling process.

SECOND SAMPLE, taken out at 1 p.m.

This sample contained the following quantities of carbon and silicium.

	First Analysis.	Second Analysis.	Mean.
Carbon	2.910	2.900	2.905
Silicium	0.226	0.168	0.197

It had the same white silvery appearance as No. 1, but with this difference, that it was slightly malleable under the hammer, instead of being brittle like No. 1. The scoria also is on the upper surface of the mass when cold, and not mixed with the metallic iron as in preceding samples.

THIRD SAMPLE, taken out of the furnace at 1 5 p.m.

The mass in the furnace having become very fluid and beginning to swell or enter into the state called "the boil," a small quantity was ladled out. The appearance of the sample when cold was quite different from that of the two previous ones, being composed of small globules adhering to each other and mixed with the scoria; the mass therefore was not compact like the former ones, but was light and spongy, its external appearance was black, and the small globules, when broken, presented a bright metallic lustre, and were very brittle under the hammer.

We had, for some time, considerable difficulty in separating the scoria from the globules of iron, but we found that by pulverizing the whole for a long time, the scoria was reduced to impalpable powder, and by sieving we could separate it

from the iron, which was much less friable. The iron thus cleansed from its scoria gave us the following results:—

	First Analysis.	Second Analysis.	Mean.
Carbon	2.466	2.421	2.444
Silicium	0.188	0.200	0.194

FOURTH SAMPLE, taken at 1 20 p.m.

As soon as the last sample had been taken out the damper of the furnace was slightly raised, so as to admit a gentle current of air, which did away with the smoke which had been issuing from the puddler's door, and a clear and bright flame was the result. This was done, no doubt, to facilitate the oxidation of the carbon of the iron, and to increase this action the puddler quickly agitated the mass. Under these two actions the mass swelled up rapidly, and increased to at least four or five times its original bulk, and at 1 20 p.m., the mass being in full boil, this fourth sample was taken out. Whilst cooling, it presented the interesting fact, that in various parts of it small blue flames of oxide of carbon were perceived, no doubt arising from the combustion of carbon by the oxygen of the atmosphere.

It is curious that this phenomenon was not observed in the previous samples. It is due probably to the following causes: Firstly, that the pig iron having been brought by the boil to a state of minute division, offers a large surface to the action of the oxygen of the air, and thus the combination of the oxygen with the carbon of the iron is facilitated. And secondly, that at this period the carbon seems to possess little or no affinity for the iron, for one of us has often observed, that when pig iron rich in graphite is puddled, the carbon is liberated from the iron; for if a cold iron rod is plunged into the mass of melted iron in the puddling furnace, it is covered with iron and abundant shining scales of graphite carbon.

The appearance of this, No. 4 sample, was very interesting; and the best idea that we can give of it is, that it is

so light and formed of such minute granules, as to be exactly like an ant's nest. The particles have no adherence to each other, for by mere handling of the mass it falls into pieces. This is due to each particle of iron being intimately mixed with scoria.

The granules of iron have a black appearance externally, are very brittle under the hammer, and when broken present a bright silvery metallic fracture.

The scoria was separated by the method above described for No. 3, and the quantities of carbon and silicium which the iron contained were as follows:—

	First Analysis.	Second Analysis.	Mean.
Carbon	2.335	2.276	2.305
Silicium	0.187	0.178	0.182

FIFTH SAMPLE, taken at 1 35 p.m.

This sample is a most important one in the series, as it is the first in which the iron is malleable and flattens when hammered. It was ladled out of the furnace just as the boil was completed and the swollen mass began to subside. The damper at the top of the chimney was drawn up, so that a very rapid draught was established through the furnace. The puddler also changed his tool, leaving the rubble and taking the puddle to work with.

When cold it partakes of the appearance of Nos. 3 and 4 samples, the mass being spongy and brittle as in No. 4, but less granulated, and like No. 3 being in separate globules, mixed with the scoria. The granules are black externally, but are bright and metallic when flattened. The analysis of these globules proves that the mass of iron in the furnace has lost, during the quarter of an hour which has elapsed since the taking of No. 4 sample, a large proportion of its carbon equal to 20 per cent. of its weight, whilst the silicium on the contrary has remained nearly stationary.

	First Analysis.	Second Analysis.	Mean.
Carbon	1.614	1.681	1.647
Silicium	0.188	0.178	0.185

SIXTH SAMPLE, taken at 1 40 p.m.

The reason why this sample was taken only five minutes after the last sample, was that the mass in the furnace was rapidly transforming itself into two distinct products, viz., the scoria on the one hand and small globules of malleable iron on the other. We attached some importance to this sample, as the workman was on the point of beginning the balling or agglomerating the globules of iron, so as to form large balls of about 80 lbs. weight to be hammered and rolled out into bars. Whilst the mass taken out for analysis was cooling, small blue flames of oxide of carbon issued from it. These were similar to those observed in Nos. 4 and 5, but were not so abundant.

The appearance of this sample was similar to the last one, with the exception that the scoria was not so intimately mixed with the globules of iron, and that these were larger and slightly welded together when hammered. The proportions of carbon and silicium were as follows :—

	First Analysis.	Second Analysis.	Mean.
Carbon	1.253	1.160	1.206
Silicium	0.167	0.160	0.163

When these figures are compared with those of the previous analysis, it is interesting to observe that whilst the silicium remains nearly stationary the carbon rapidly diminishes, for in the five minutes which elapsed between the taking out of the two samples, there are 28 per cent. of the carbon burnt out. This rapid decrease of carbon in the iron is maintained during the remaining ten minutes of puddling. In fact, in one quarter of an hour, viz., from 1 35 to 1 50 the iron lost 50 per cent. of the carbon.

SEVENTH SAMPLE, taken at 1 45 p.m.

This sample was obtained when the puddler had begun to ball. The appearance of the sample, although similar to the

last, differs from it by the granules being rather larger and nearly separated from the scoria, which forms a layer at the top and bottom of the mass.

These granules are also much more malleable, for they are easily flattened under the hammer. This last fact is easily accounted for by the small amount of carbon which it contains, as stated above and shewn by these results.

	First Analysis.	Second Analysis.	Mean.
Carbon	1.000	0.927	0.963
Silicium ...	0.160	0.167	0.163

EIGHTH SAMPLE, taken 1 50 p.m.

This last sample was taken a few minutes before the balls were ready to be taken out of the furnace to be placed under the hammer, and was a part of one of the balls which was separated and placed to cool.

It was observed that no blue flame issued from the mass as it cooled. The appearance of the sample shewed that the mass constituting the ball was still spongy and granulated, similar to the previous ones. The only difference was that the granules adhered together sufficiently to require a certain amount of force to separate one from the other, and also that they were much more malleable under the hammer. They were found to contain the following quantities of carbon and silicium, per cent. :—

	First Analysis.	Second Analysis.	Mean.
Carbon	0.771	0.773	0.772
Silicium	0.170	0.167	0.168

We should observe here that the black coating which covers the granules of iron, even of No. 8 sample, preserves the iron from all oxidation, for none of the samples became oxidized during the nine months they were in the laboratory exposed to the atmosphere, and to the various acid fumes floating about. This black coating is probably composed of a saline oxide of iron.

NINTH SAMPLE OF PUDDLED BAR.

The balls taken out of the furnace were hammered and then rolled into bars, and in these we found the following:—

	First Analysis.	Second Analysis.	Mean.
Carbon	0.291	0.301	0.300
Silicium	0.130	0.110	0.120
Sulphur	0.142	0.126	0.134
Phosphorus	0.139	...	0.139

TENTH SAMPLE—WIRE IRON.

The puddled bars were cut into billets of about four feet in length, and heated in a furnace to white heat, and then rolled into wire iron. The proportions of carbon, silicium, sulphur, and phosphorus, were as follows:—

	First Analysis.	Second Analysis.	Mean.
Carbon	0.100	0.122	0.111
Silicium	0.095	0.082	0.088
Sulphur	0.093	0.096	0.094
Phosphorus,	0.117	...	0.117

To complete the series of products in the conversion of pig iron into wrought iron, we analysed the scoria or slag which remained in the furnace after the balls had been taken out, and found its composition to be as follows:—

Silica	16.53
Protoxide of Iron	66.23
Sulphuret of Iron	6.80
Phosphoric Acid	3.80
Protoxide of Manganese	4.90
Alumina	1.04
Lime	0.70
	<hr/>
	100.00
	<hr/>

Therefore, in the scoria are found the silicium, phosphorus, sulphur, and manganese, which existed in the pig iron; and probably the phosphorus and silicium are removed from the iron by their forming fusible compounds with its oxide.

We shall conclude this paper by giving our results in a tabulated form, so that the removal of the carbon and silicium

may be better appreciated by those who may consult it, with the view of obtaining such information as may lead them to those improvements to which we think our investigations tend.

		TIME.	CARBON.	SILICIUM.
Pig Iron used		12.0.	2.275	2.720
Sample No. 1		12.40 P.M.	2.726	0.915
" 2		1.0. "	2.905	0.197
" 3		1.5. "	2.444	0.194
" 4		1.20 "	2.305	0.182
" 5		1.35 "	1.647	0.183
" 6		1.40 "	1.206	0.163
" 7		1.45 "	0.963	0.163
" 8		1.50 "	0.772	0.168
Puddled Bar 9			0.300	0.120
Wire Iron 10			0.111	0.088

Finally, we wish to express to Mr. Siméon Stoikowitsch our best thanks for the ability and perseverance which he has shown in helping us in these long and tedious analyses.



Crace-Calvert, F. and Johnson, Richard Irwin. 1857. "The Chemical Changes which Pig Iron Undergoes during its Conversion in to Wrought Iron." *Memoirs of the Literary and Philosophical Society of Manchester* 14, 121–136.

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