to be under 0·04 per cent., it is absolutely necessary to use either Swedish iron, washed metal, or one or two very special brands of English iron.

Many steel makers prefer, in the case of *axle steels*, which usually contain from ·25 to ·35 per cent. of Carbon, to catch the metal when the required point of decarburisation has been reached, rather than work down to nearly soft steel and then recarburise by charging pig-iron on the banks. When making steel *below 0·4* Carbon, most excellent results can be obtained by this method of working, and the difficulties of getting slag and metal into the right condition are considerably less than in case of higher Carbon steel; but even for these lower Carbon steels it is necessary to use a larger percentage of pig-iron to ensure a fairly long boil than if it is intended to recarburise in the furnace, and not more than 50 per cent. of scrap should be used in the charge.

In the manufacture of special steels or alloys for armour plates and other purposes, the charge is worked in the same way as for ordinary high Carbon charge, and then the special alloy of Ferro-Chrome, Nickel, &c., added, special care being taken to see that the slag is as free as possible from oxides. The ingots of these steels are usually cast from the bottom, to ensure greater soundness and a better surface or skin on the ingot.

CHAPTER VIII.

BASIC SIEMENS PROCESS.

THE basic Siemens process, like the basic Bessemer process, depends, for the removal of Phosphorus, entirely on the formation of stable Phosphates, and this is effected by lining the furnace with a basic or neutral material, and by lime additions during the working of the charge. The furnace employed, with the exception of some minor details, is identical with that used in the acid process, and the method of working is the same, the impurities being oxidised partly by the air during the melting, and partly by the addition of solid Oxides of Iron to the molten bath after the charge is melted.

Early Practice.—In the early days of the basic Siemens process several furnaces were specially designed to meet the particular difficulties encountered, to facilitate repairs, &c., and to reduce the cost of construction; but after many trials it has been found that a furnace constructed on modern lines similar to that used for acid work gives the best all-round results in actual practice.

The Batho Furnace.—Amongst the earliest forms of modified furnaces used for basic work was the Batho furnace, which was greatly improved in various ways by Messrs. Riley, Dick, Wailes, and Hilton. In its earlier form it was a round furnace, and the roof was built in an iron frame, forming a lid, and was suspended independently of the walls of the furnace from girders above, arrangements being made for raising the roof bodily when the furnace required re-lining or repairs. A sketch showing the general arrangement of a modified form of the furnace of this type is given in figs. 158 and 159. The chief points urged in favour of these furnaces were, that the regenerators, being on each side of the body of the furnace, were quite independent of the latter and contained in separate iron casings so that in the event of a breakout there was no risk of the metal getting into the regenerators; that it was impossible for a leakage of gas to take place between the gas and air regenerators, leading to the destruction of the brickwork; and that, the regenerators not being underneath the staging, the latter was much cooler for the men to work on. One modification of the furnace was to make the body elliptical (as shown in the sketch) instead of cylindrical, but with all these furnaces the difficulty of getting the gas and air ports to withstand contraction and expansion was so great that it has been found better to return to the rectangular furnace, with a solid square block for the ports, which is capable of resisting the great strain put upon it by contraction and expansion. The modern type of furnace (as shown in figs. 127-130) practically has all the advantages claimed for the Batho furnace. The body of the furnace is independent of the regenerator arches; the regenerators are away from the bottom of the furnace, and there is practically no risk of air and gas burning, due to leakage of gas and air between the regenerators. It may be, therefore, taken as established by experience that the best form of furnace for basic Siemens work is that of the ordinary Siemens type, as far as general design is concerned, and it will differ only in the internal lining of the hearth or crucible, and the method of supporting the roof and other details. Owing to the very friable nature of basic material, it is not possible to build the entire working body of this; it would,

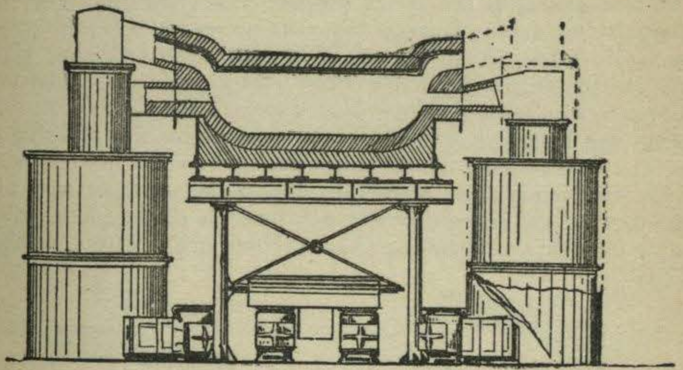

Fig. 158.

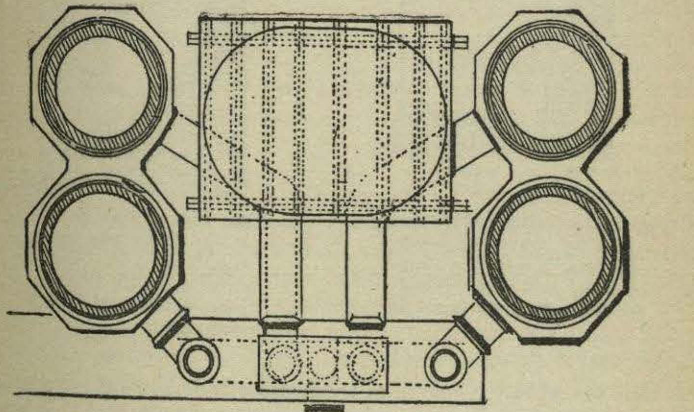

Fig. 159.—Sketches illustrating general arrangement of a Batho Furnace. Sectional plan and elevation.

for instance, be quite impossible to build the roof with basic bricks, or even the entire walls, as they would not support the weight of the roof, and consequently part of the structure has to be of basic and part of acid materials. There is thus the danger of these two dissimilar bodies fluxing when in contact at high temperatures. It was to overcome these difficulties that the suspended roof of the Batho-Wailes furnace was designed, but it has been found that these difficulties of the fluxing of the two materials are not so serious in practice as theoretical consideration might lead us to suppose, and they have been successfully dealt with by practical men. It was discovered, when the basic Siemens process began to be adopted, that silica bricks of best quality might be in contact with basic material without any serious fluxing action, *provided they were not subjected to pressure.* This fact was soon taken advantage of, additional security being given by generally introducing a joint of some neutral infusible material like Chrome iron ore to form a neutral joint between the two bodies.

Lining the Furnace.—Probably the most simple way of lining a basic Siemens furnace is to build up the entire casing, from the bottom, with acid bricks, the roof being then carried by the walls, as in an acid Siemens furnace. The hearth, or crucible of the furnace, is then padded with basic material, to a height above the slag line, as shown in fig. 160. The objection to this is that the working hearth of the furnace is somewhat restricted, and a furnace which, in acid work, would take 25 tons, will probably not take more than 20 tons; provided one is prepared to go to the extra first cost, and build larger furnaces, this system is probably the best as regards repairs, as in the event of the banks being cut away, if they are not fluxed quite to the Silica brickwork backing, there is no fear of roof or side walls giving way. Another method of relieving the basic material from the weight of the walls of the furnace, is to partly support the side walls, just above the basic material, by a stout angle iron, *a*, rivetted upon the inside of the furnace casing, as shown in fig. 161,, and to make a joint of Chrome iron ore between the acid and basic materials. A method, originally used by Mr. Darby, of Brymbo, and shown in fig. 163, is one which has been very generally adopted, and is found to give very good results, and when the question of output for a given size of furnace is considered, perhaps better results than any other. This, as will be seen from figs. 162 and 163, consists in carrying the weight of the roof on a long horizontal arch, so that at the point of contact there is no great pressure between the acid brickwork and basic material, and under these conditions, even without a Chrome joint, little or no fluxing takes place between the two materials.

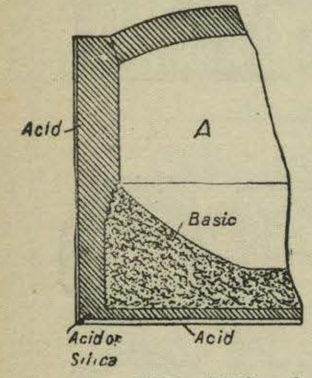

Fig. 160. — Silica Brickwork continued down to bottom of hearth to carry the weight of walls and roof. Hearth padded with basic material.

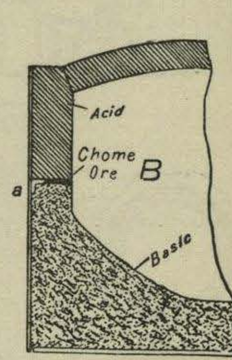

Fig. 161.—Silica Brickwork above the basic supported on angle iron, *a*, with Chrome joint between the two materials.

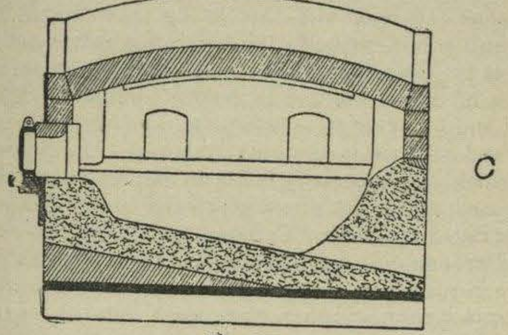

Fig. 162.

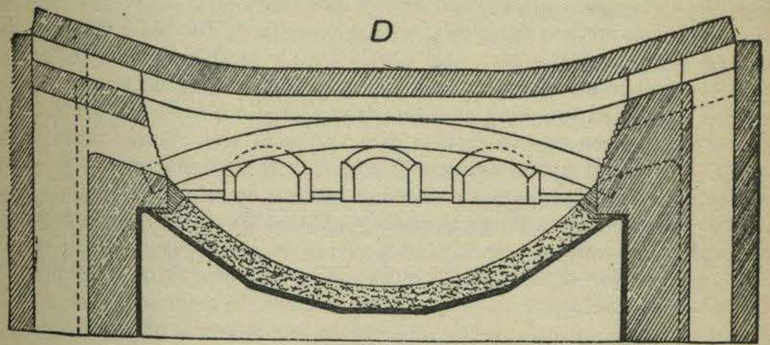

Fig. 163.

Preparing the Hearth.—In making the hearth or bottom of the basic Siemens furnace, several methods are in use. In some of the earlier furnaces the hearth was built up with basic bricks (see p. 59), made either by hand or in a hydraulic press, with tar as binding material, and the joints were then slurried with a mixture of basic material and tar; this was not found to give good results, as not infrequently if the bottom got cut away, large portions of it would lift, and a number of bricks float up into the bath of metal. Another method tried was ramming the entire bottom up with basic material and tar, as used for lining converters, and then gradually heating the furnace, first with a fire on the hearth, and then with the gas, until the entire mass was burnt hard. In this case, as with bricks, it was found practically impossible to burn the basic material hard through its entire thickness, with the result that if the bottom got cut away to any depth, to the partially burnt lower portion, large masses would lift. By far the best practice is to glaze the bottom on, as in the case of the acid furnace. It is usually best before starting to cover the iron bottom plates with two or three courses of Silica bricks,* and then a few inches of ramming of basic material mixed with tar; this is then well fired until burnt quite hard, when a thin layer of basic material, either dry or mixed with a little tar

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* Magnesia brick may with advantage be used for larger furnaces, but are much more expensive.

and not exceeding an inch in thickness, is thrown into the furnace, levelled with the peel, and well glazed on. This is repeated until the bottom is built up to the required thickness and shape. To get the required thickness on the banks, basic bricks may be placed round the sides of the furnace, in a similar way to that shown in fig. 144, for an acid furnace, or a thicker layer may be rammed on. Burnt Magnesite has been used very successfully as a lining for Siemens furnaces, and this lining lasts much longer than an ordinary basic lining, but, owing to the high price, it has not been generally adopted, and it is probable that it is economical to use it only when situated so that supplies of Magnesite can be readily obtained. Magnesite bricks have been used and found most satisfactory, especially as a backing for the basic material, and expense is the only drawback. In America, in parts of the furnaces which are especially liable to be cut away, these bricks are very generally used, and if not directly exposed to the fluxing action of the slag, last for an indefinite time. Carbonate of Magnesia, containing about 98 per cent. of Carbonate, is used for making these bricks.

In some American works the practice is to put first a course of fire-bricks and then Magnesia bricks, and then glaze basic material on to these to form the hearth. In others the first course is fire-brick, then one course of Chrome bricks, then Magnesia bricks, and finally basic material.

Chrome iron ore has been used alone as a lining for basic furnaces, but partly on account of the cost, and partly owing to the difficulty of getting it to frit together and form a hard mechanically strong bottom, its use is practically confined to acting as a separating medium between silicious and basic material when one is resting directly upon the other. Bauxite has also been tried, but unless extremely pure is not sufficiently infusible, and, owing to its great shrinkage on intense heating, is liable to crack. Lime, which is the cheapest and most readily obtainable of all basic or neutral materials, is not suitable, partly on account of its great infusibility, and partly owing to the difficulty of keeping it for any length of time previous to use without slaking.

As a matter of actual practice, therefore, no material has been found so generally suitable as the burnt dolomite or basic material, as it is sufficiently infusible for the purpose, and at the same time sufficiently fusible to just frit together and form a hard mechanically strong bottom at Siemens furnace temperatures. It must be remembered that, from the chemical point of view, any of these so-called neutral materials—*i.e.*, materials that are inert or not readily acted upon, either by ferruginous or basic slags—would answer perfectly for the hearth of the furnace, the only thing required being a material to act as a crucible, which shall be infusible and unacted upon by highly ferruginous and calcareous slags, at the temperature employed, and so enable lime to be added to form a stable Phosphate. The tapping-hole in a basic Siemens furnace is made in a manner very similar to that in an acid Siemens, anthracite being placed at the back, but instead of fireclay and sand, a little basic material and tar are generally rammed into the hole, next to the anthracite, and the remainder made up on the outside with sand.

Details of Working.—The usual method of working is as follows:—The furnace being thoroughly hot, generally a little lime and ore are charged upon the bottom, then the pig-iron, with which a few shovelfuls of ore and lime are mixed from time to time, and, lastly, the greater portion of the scrap. In the case of very light scrap, a portion of this may be charged during the melting down, as in the acid process, but it is preferable to charge all the pig and scrap at the same time. The charge is then melted down, and when clear—*i.e.*, quite melted—additions of iron ore or non-silicious oxide from basic or oxide reheating furnaces, or any form of Ferrous or Ferric Oxide, free from Silica, are thrown in, with lime or limestone from time to time. The furnaceman, when the charge has been on the boil for some time, takes out small samples with the spoon, hammers them down, quenches, and bends them over until fracture takes place, and from the fracture and the condition of the slag is able to judge how the process is proceeding, and if more ore or lime is required. Although it is essential to maintain a basic slag, and also a fairly oxidising one during the early stages of the process, it is important that too much lime should not be added, both on the score of economy, and also to avoid getting a pasty slag; and it is equally important not to have too oxidising a slag, as otherwise the metal will be over-oxidised, very wild in casting, and probably red short when rolled. The great point which the furnaceman has to guard against is the removal of his Carbon before the Phosphorus, and this is especially so in the case of high Phosphoric charges, as there is often a tendency for the metal to go off the boil before the Phosphorus is oxidised to the required extent. If this happens it is only with the greatest difficulty that the last traces of the Phosphorus can be finally removed. If this should occur, the only thing to do is to add hematite pig-iron to the bath, and try to get the metal on the boil again. The probable reason why it is so difficult to remove Phosphorus after the Carbon has been oxidised is that there is no CO coming off from the bath to act as a mechanical stirrer, and bring the metal into intimate contact with the oxide and lime in the slag, by which the Phosphorus is oxidised, and unites with the lime to form a stable Phosphate of Lime. In working highly Phosphoric charges, as in the case of a very high Phosphoric pig-iron and small percentage of scrap, this removal of the Carbon before the Phosphorus is much more liable to occur than in working low Phosphoric pig and the usual amount of scrap, as the relation between the percentage of Carbon to the percentage of Phosphorus is so much lower in the former, and consequently the risk of removing the Carbon before the Phosphorus so much the greater. The furnaceman should never tap until he is satisfied from the examination of his samples that his Phosphorus is not more than ·05 per cent., as otherwise he may find an average sample from the heat when tapped gives over ·06 per cent. In some works a sample passer makes a rapid determination of Phosphorus by the Molybdate method, measures the precipitate in a very small tube of known size and compares it with a standard sample, this being an excellent check on the furnaceman.

Although the reactions taking place in the basic Siemens process are practically identical under different systems of working, the rate of removal of the metalloids may be made to vary within very wide limits. As Oxide of Iron does not readily flux with the basic bottom in the way it does with a silicious hearth, considerable quantities of Oxide can be placed on the bottom of the furnace before charging, and in the very early days of the basic Siemens process, the author believed that the rapidity of the working of charges might be greatly facilitated by adding a large proportion of the Oxide and lime or limestone required on the bottom of the furnace before charging the metal. By this method of charging, during the melting period, the metal runs down into a bath of molten basic Oxide, and the impurities are rapidly removed from one part of the charge while the other is melting, so that, when completely melted, the charge is nearly converted into steel. Although this was found to be the case under the special conditions of the experiments made, which were with very high Phosphoric pig-iron, it was also found that there was great liability to get the Carbon removed before the Phosphorus. What probably happened was that as the metal melted little by little into the molten Oxide, the Carbon was oxidised very rapidly, and before the charge was entirely melted, there was practically a bath of carbonless and dephosphorised steel, and as further pig-iron melted down, this Phosphoric material mixed with the bath of practically carbonless iron. The result was metal comparatively high in Phosphorus and low in Carbon, and there was then great difficulty in removing the last traces of Phosphorus. With a low Phosphoric pig-iron, where the proportion of Carbon to Phosphorus would have been higher, much better results could have been obtained, and even with high Phosphoric iron, containing 2·5 and 3·0 per cent., some hundreds of tons of excellent steel were made.

The removal of Phosphorus before the Carbon in the Siemens furnace is largely a question of temperature, and it was found in practice that the temperature of the furnace when working on these lines could not be controlled sufficiently to insure the removal of the Phosphorus before the Carbon, with the result that the production of low Phosphorus steel regularly could not be depended upon, and more regular results were obtained by adding less Oxide before charging, and finishing the charges by addition of Oxide after the bath was melted. In some works no Oxide is charged with the metal, but the usual practice is to add some, the amount varying with the composition of the charge. It is not possible to lay down any definite rule as to the amount of Oxide which should be added with the charge, as it is really a matter of experiment to find the proportion that gives the best practical results, both as regards rapidity of production and quality of product for a given composition of charge.

When the furnaceman, by examination of his samples, is satisfied that the Phosphorus and Carbon are removed to the required degree, he at once gets ready to tap. A few half pigs of hematite iron are added to bring the metal to the boil again, and the tapping-hole is opened by driving a steel bar through it as described in the acid process. The Ferro-Manganese is always added in the ladle, usually broken to the size of peas, and thrown on the stream of metal as it passes from the furnace. If added in the furnace, there is great danger of Phosphorus passing back from the slag to the metal.

Pig-iron and Scrap.—The pig-iron used should be as low as possible in Silicon and Sulphur, fairly high in Manganese, and Phosphorus may vary from 0·100 to 2·00 per cent., or even 3·00 per cent., although a pig-iron not exceeding 1·5 per cent. is much to be preferred, if it is desired to produce regularly a steel of high quality.

Unlike the basic Bessemer—where a certain amount of Phosphorus is required to maintain the heat of the bath—here, where the temperature is maintained largely by external means, the lower the percentage of Phosphorus in the pig-iron used, the greater the ease and regularity with which this impurity can be removed. The actual charge of pig-iron and scrap will vary with the quality of the materials available.

In many works in England, a pig containing Phosphorus about 1·75 per cent., Silicon under 1·00, Sulphur, ·05; Manganese, 1·5 to 2·00, and Carbon 3·50, is very generally used, and about 25 to 30 per cent. of wrought iron and steel scrap is charged with this pig. More scrap may be used if available; but, when working on a large scale, it is not generally possible to obtain more at a price which will pay in this country.

One great advantage of the basic Siemens over the acid process, is that miscellaneous scrap, either wrought iron or steel, containing a percentage of Phosphorus which would render it useless for acid Siemens practice, may be used, and, consequently, this can be obtained, often at a lower price than selected steel scrap, and a larger proportion can be used in the charge. In some cases, in districts where large quantities of scrap are obtainable, as much as 70 to 80 per cent. is melted in each charge, and then very rapid working is possible, as much as three to four heats being melted in the twenty-four hours; in these cases, the furnace becomes really only a scrap melting furnace, the whole of the impurities being practically removed during the melting period so that when once the bath is clear it is ready to tap, provided it is sufficiently hot. This practice is followed in some parts of the Continent by small works with one or two furnaces, in districts where large quantities of scrap can be cheaply obtained; but commercial conditions do not permit of its being carried out in England to any extent.

The following analyses (Table xxxii.) made by the author from a number of charges, illustrate the removal of impurities in the basic Siemens furnace during melting, when charging varying quantities of ore with the pig-iron; charges B may be taken as fairly typical of normal working for high Phosphorus pig, about 2 cwts. of ore or oxide being charged per ton of metal with the pig-iron. For a low Silicon and Phosphorus charge, of course, the amount of ore would be considerably reduced to obtain the same percentage of removal of the impurities:—

TABLE XXXII.—SHOWING THE REMOVAL DURING MELTING OF METALLOIDS IN BASIC OPEN HEARTH UNDER DIFFERENT CONDITIONS OF WORKING.

Composition of Charge. Calculated. 20 per cent. Scrap.		WHEN MELTED.						
		A. 1 Cwt. of Oxides per Ton of Metal charged with the Pig-iron.				B. 2 Cwts. of Oxides per Ton of Metal charged with the Pig-iron.		
		1	2	3	4	1	2	3
Carbon,	3·00	2·38	2·40	2·29	2·49	1·89	1·69	1·59
Silicon,	1·40	·069	·060	·046	·093	·046	·074	·046
Phosphorus,	2·80	2·67	2·43	2·44	2·48	1·588	1·64	1·32
Manganese,	1·80	·546	·89	·600	·66	·100	·04	·08
Sulphur,	·060	·06	·052	·032	·071	·096	·104	·096

Same quantity of Lime charged with heats 1, 2, 3, 4.

Composition of Charge. Calculated. 20 per cent. Scrap.		WHEN MELTED.							
		C. 3 Cwts. of Oxides per Ton of Metal charged with Pig-iron.				D. 4¾ Cwts. (practically the whole quantity required) of Oxides per Ton of Metal charged with the Pig-iron.			
		1	2	3	4	1	2	3	4
Carbon,	3·000	1·00	1·300	·670	0·900	0·140	0·120	0·150	0·130
Silicon,	1·36	·037	·040	·037	·040	·090	·020	·016	·046
Phosphorus,	1·70	·600	·640	·705	·960	·134	·088	·122	·081
Manganese,	1·14	·288	·288	·200	·140	·288	·200	·140	·160
Sulphur,	·140	·139	·140	·120	·107	·127	·160	·150	·150

Same quantity of Lime charged with heats 1, 2, 3, 4.

It will be noted that, when a large quantity of ore was charged with the metal, the bath was practically decarburised and dephosphorised when melted.

Considerations Respecting Slag.—The most essential conditions for the successful working of the basic Siemens process are :—1. The maintenance of a sufficiently basic slag to prevent the dissociation of the basic Phosphate of Lime by the reducing action of the Carbon in the metal bath, and of the Silica in the slag. 2. To prevent fluxing of the bottom by a too silicious slag. 3. To maintain a slag sufficiently fluid, so that it may be brought into intimate contact with the metal. 4. To keep the slag sufficiently, but not too oxidising, to do the necessary chemical work during the early stages of the process, and to finish with as neutral a non-oxidising slag as possible. This latter is very important, as an oxidising slag at the end of the operation means over-oxidised metal, which leads to wild heats, and to finished steel which is red short and mechanically defective. Basicity of the slag is obtained by the lime or limestone additions, and by the basic material which is taken up from the lining, although one great object of the lime additions is to prevent the latter as much as possible. The fluidity is due largely to the Manganese oxidised, the Oxide of Iron formed during melting, and added as iron ore, and any other small quantities of bases, added as impurities in the ore and lime, which unite with the Silica present. It is mentioned by Campbell,* who gives a large number of analyses from different charges with varying percentages of Phosphorus to support his contention, that as the Silica decreases the **FeO** increases, and that under similar conditions low Silica means high **FeO**, and consequently more complete dephosphorisation.

He suggests that the reason for this automatic adjustment between the Silica and the Oxide of Iron is due to a struggle to attain a certain degree of fluidity, and acting in obedience to this tendency, Silica and Oxide of Iron replace each other. Whether the more complete dephosphorisation is due simply to increased fluidity or to the oxidising power of the slag, Campbell considers has not been decided; but it seems probable it is due to both these causes, as greater fluidity means more intimate contact with the metal, the larger percentage of Oxide means a more energetic, oxidising slag, and less Silica means a relatively more basic slag, with greater power of retaining the Phosphorus in the form of stable Phosphate of Lime. We thus have the Oxide of Iron in the best possible condition to do its work of oxidation, and a slag rich in lime ready to combine with this Phosphorus when oxidised, which broadly may be taken as the functions of these two bodies in basic Siemens practice. In fact the successful working of the process and production of steel of regular quality may be said to practically depend upon maintaining the proper adjustment between the oxidising bases in the slag on the one hand, and the non-oxidising bases on the other, and it is here that the skill of the melter shows itself. The following are some typical analyses of basic slags from basic Siemens furnaces, taken from an average of a large number of analyses. The Phosphoric acid will vary with the amount of Phosphorus present in the original charge, but the Silica and lime will be relatively about the same, as the amount of lime added depends far more upon the Silicon content of the charge than the Phosphorus content, and the Silicon varies comparatively little except in cases where almost entirely scrap charges are being worked. Thus in actual practice the additional amount of lime it is necessary to add to a charge containing 2 per cent. Phosphorus, as compared with a charge with 1 per cent., does not greatly affect the relative percentages of Silica and lime in the two slags.

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* *Trans. American Inst. of Mining Engineers*, vol. xxii., pp. 445 and 446.

The following may be taken as fair average composition of finishing slags :—

Composition of Basic Slags Taken from a Large Number of Casts.

Silica.	Oxide of Iron.	Oxide of Manganese.	Lime.	Magnesia.	Phosphoric Acid.
12·89	16·85	7·54	41·4	4·70	11·2

Campbell,* in his paper on the open hearth process, gives the following average composition for slags :—

Silica.	Oxide of Iron.	Phosphoric Acid.	Oxide of Manganese.	Lime.	Magnesia.
10·50	17·65	13·06	8·75	40·84	5·04
11·50	15·57	13·12	10·22	40·02	5·47

The final slag should not contain more than 16 to 17 per cent. of Oxide of Iron, as more than this usually means undue waste and liability to over-oxidised metal.

Manufacture of High Carbon Steel in Basic Siemens Furnace.—When using Phosphoric pig, &c., in the basic open hearth, it is difficult to completely remove the Phosphorus before the Carbon and finish with a bath of any required content of Carbon, and it is not possible to pig back by charging hematite pig-iron on the banks of the furnace to give the percentage of Carbon required, as in the acid process, as this would reduce phosphoric acid from the slag, and the Phosphorus would pass back into the metal. If it is desired to make high Carbon steel, the usual practice is to recarburise the metal outside of the furnace, and so keep the slag and Carbon out of contact.

Darby Recarburising Process.—Mr. J. H. Darby, of Brymbo, some years ago, taking advantage of the fact that molten steel rapidly absorbs Carbon when brought into contact with it, devised a special method of making steel of any required Carbon percentage by intimately mixing Carbon with the molten metal as it leaves the furnace.

The arrangement used is shown in fig. 164. It consists of a hopper with an adjustable orifice, in which the required weight of Carbon is placed and allowed to fall in a stream into the subsidiary perforated vessel, A, which is suspended over the casting ladle, and into which the steel flows on its way to the ladle. The delivery of the Carbon can be regulated by varying the opening in the hopper, and only small quantities of Carbon and steel coming together at one time, there is no danger of causing a boil in the ladle, and intimate admixture of Carbon and steel is insured. The whole of the Carbon is not absorbed, there being a loss of about 20 per cent., which must be allowed for in calculating the amount required for any particular charge.

The Carbon used should be as dense as possible and free from Sulphur, anthracite coal or dense, hard, pure coke giving good results.

Steel is now generally carburised by adding anthracite coal in the ladle, or throwing it on the stream of metal as it passes into the ladle; in this way the carburisation can be fairly well controlled, but care must be taken to add the Carbon before the slag passes into the ladle or it is liable to cause the metal to boil.

The Elimination of Sulphur.—Under the normal conditions of working the basic Siemens process, the removal of Sulphur is very variable—in some charges, considerable amounts being removed, and in others, worked apparently under the same conditions, none at all, and even an increase is sometimes observed. It is advisable, therefore, if a regular low Sulphur steel is desired, to start with low Sulphur pig, and a pig containing also a fair percentage of Manganese.

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* *Trans. American Inst. of Mining Engineers*, vol. xxii., p. 440.

The exact part played by Manganese in the elimination of Sulphur in the basic Siemens may not be clearly understood; but that it does play an important part has been proved without doubt, and the addition of Spiegel or Ferro-Manganese at the end of the charge before tapping is generally followed by a distinct reduction of Sulphur. It is probable that the Sulphur passes into the slag in the form of Sulphide of Manganese in the same way

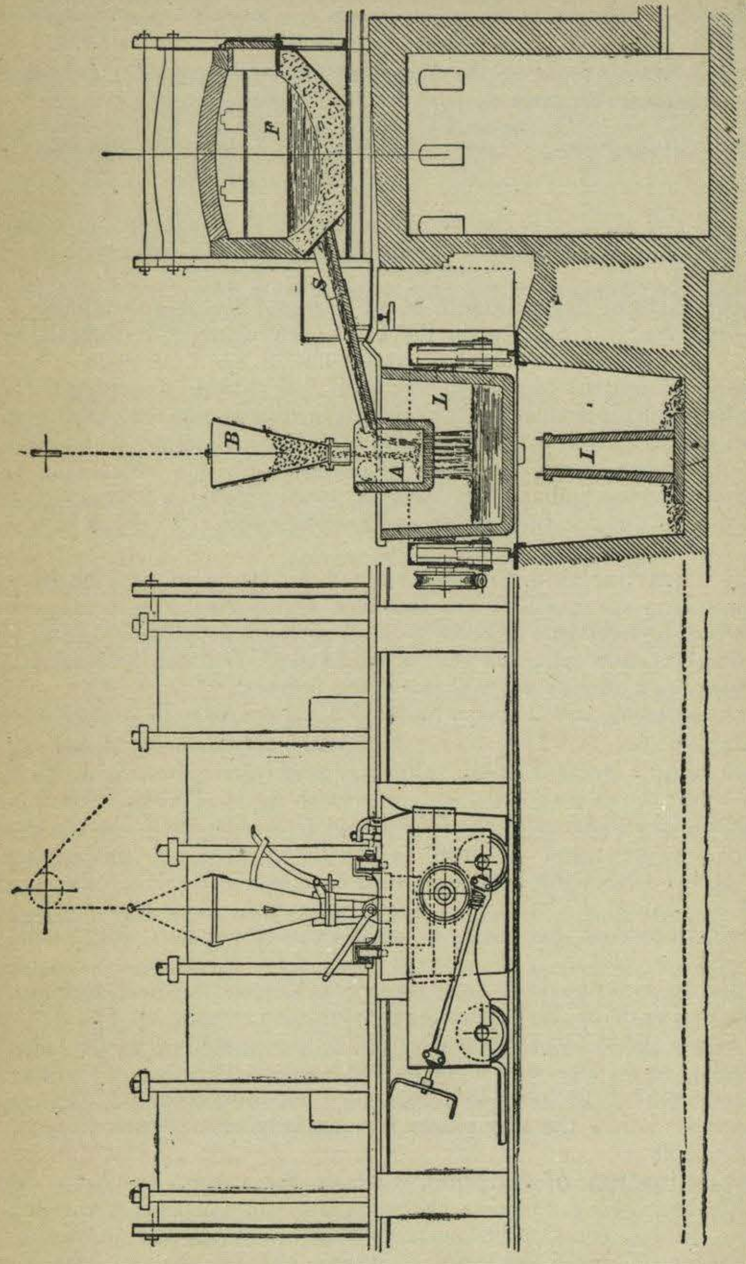

Fig. 164 - Darby Recarburising Apparatus—B, Hopper containing Carbon; A, subsidiary vessel for mixing Carbon and steel before entering ladle; L, ladle; I, ingot mould.

The subsidiary vessel, A, is now rarely used, sufficient intimate admixture and absorption of the Carbon being obtained by allowing the Carbon to fall in a fine stream upon the metal as it flows from the furnace into the ladle.

as it was shown by Massenez* to do in a metal mixer in the presence of Manganese. The amount of Sulphur which can be removed by Manganese *additions* is, however, very limited, as, if too much carburising metal is added, Phosphorus will be reduced from the slag and pass back into the metal, and the steel will be high in Phosphorus. It is better, therefore, to melt a certain proportion of manganiferous pig-iron with the charge, or to add manganiferous ores to the bath to maintain a fair percentage of Manganese Oxide in the slag, which is alternately reduced and oxidised, and, in passing backwards and forwards from the metal to the slag, certainly tends to remove the Sulphur, especially when a very basic slag is employed. Campbell has shown in his paper already referred to that, other things being the same, a highly calcareous slag distinctly tends to the more complete removal of Sulphur, and, broadly, the more basic the slag the larger the percentage of Sulphur removed. Here, again, the results are very variable, and it seems impossible to rely upon the removal of a definite percentage of Sulphur, even when working under the same conditions as regards slag and metal.

Various methods of desulphurising molten metal before or during conversion into steel have been suggested, the essential conditions in all apparently being a fluid basic slag and intimate contact between metal and slag.

Rollet claimed to be able to remove 99 per cent. of the Sulphur by melting pig-iron with large excess of lime, and from 2½ to 4·8 per cent. of Fluorspar, so that the slag contained less than 2 per cent. of Silica. Under conditions of low temperature, Oxide of Iron, as shown by the puddling and Bell and Krupp washing processes, is capable of removing very considerable quantities of Sulphur, varying from 50 to 90 per cent., according to the percentage present, and other conditions. The old Henderson process of pouring molten pig-iron on to the hearth of a furnace covered with fine Oxide of Iron and Fluorspar, removed considerable quantities of Sulphur, and the Heaton process of pouring molten iron on to nitrate of soda, according to the analyses of Miller and Snelus, was most effective in removing it. As much as 77 per cent.† of the Sulphur can be removed by pouring molten iron on to a mixture of soda ash and ground limestone

The removal of Sulphur in the metal mixer by Manganese as MnS has already been referred to, and this is probably the most satisfactory method of desulphurising large quantities of molten metal, especially if manganiferous metal for mixing is available.

With the exception of the mixer, practically all the above methods depend upon the action of a fluid basic, and more or less oxidising, slag.

The use of alkaline salts has been shown by Messrs. Ball and Wingham to remove considerable quantities of Sulphur, and their conclusion that the absence of oxidising agents is desirable, seems to be confirmed by the results obtained in electric furnaces,‡ where it is found that a slag containing a very high percentage of lime and practically free from Oxides of Iron gives the best results.

Further experience with the basic open hearth process has demonstrated that to desulphurise, it is best first to dephosphorise as much as possible with a fairly oxidising slag, and then to add excess of lime, with fluor spar to increase the fluidity of the slag, towards the end of the operation; no further additions of oxide should be made, so that the finishing slag may contain the maximum amount of lime and the minimum of Oxide of Iron. The percentage of lime which a basic open hearth slag can be made to carry and still be sufficiently fluid is limited by the temperature available, and, consequently, the very complete removal of Sulphur is attended with considerable practical difficulties. This elimination of Sulphur is costly, as it

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* *Iron and Steel Inst. Journ.*, 1891, vol. ii., p. 76.

† *Ibid.*, 1892, vol. ii., p. 257.

‡ See chap. xi., p. 279.

is essential that the metal should be kept in the furnace under a very basic slag for a considerably longer period than would be necessary for the removal of Phosphorus to the usual limits required for structural steel, which entails a large consumption of fuel and lime and reduces the output of finished product in a given time. Probably a mixture of soda ash and finely-ground lime would give excellent results, the soda ash giving fluidity and basicity, and molten metal poured upon such a mixture, under proper conditions, would be largely desulphurised, the chief objection being the question of cost.

The Saniter Process.—The method of desulphurisation proposed by Saniter, has given very good results, and is now in use in several steel works.

It is based on the use of Calcium Chloride in conjunction with lime, and, although the exact reactions by which the Sulphur is removed are not clearly understood, the researches of Stead * and others have thrown some light on the subject, and it seems probable that an oxychloride of lime of indefinite composition is formed, which enables a slag of great fluidity and at the same time of great basicity to be brought into intimate contact with the fluid metal.

The process may be carried out in two ways—(1) by treating the molten cast iron in a ladle as it comes from the blast furnace before it is cast into pigs; (2) by desulphurising the molten metal during its conversion into steel in the basic open hearth or basic Bessemer converter.

In the first case, a fusible mixture is made by grinding together Calcium Chloride, Lime, Fluorspar, and Limestone in the proportions which are found to give a slag which is fluid at the melting point of cast iron.

This mixture is placed on the bottom of the ladle, and the molten iron run upon it, when it gradually melts and rises through the bath of molten metal, and, in so doing, removes as much as 66 per cent. of the Sulphur present from iron containing 0·20 per cent. Saniter recommends the following mixture for each ton of pig-iron:—

Dry Calcium Chloride, 9 lbs. Fluorspar, 9 lbs. Lime, 15 lbs. Limestone, 8 lbs.

In desulphurising in the basic open hearth or Bessemer processes dry Calcium Chloride must be added during the working of the charge, with the usual lime additions, care being taken that the latter are added in sufficient quantity to give a slag containing over 50 per cent. of lime. It seems probable that, given a basic slag with this percentage of lime, which, at the same time, retains its fluidity, the dephosphorisation, as well as desulphurisation, should be greatly facilitated, and the following analyses† of steel charges, made from pig-iron of very varying composition, distinctly support this view:—

TABLE XXXIII.

	1.		2. Cleveland.		3. Basic Cinder Pig.		4. Hematite Pig.	
	Pig-iron.	Steel.	Pig-iron.	Steel.	Pig-iron.	Steel.	Pig-iron.	Steel.
Carbon, .	...	0·12	...	0·25	...	0·22	...	0·110
Silicon, .	0·28	Trace	1·50	Trace	0·5	Trace	0·70	Trace
Sulphur, .	0·96	0·07	0·25	0·025	0·22	0·018	0·06	0·016
Phosphorus,	0·75	0·026	1·50	0·030	3·50	0·036	0·06	0·008
Manganese,	0·30	0·47	0·70	0·45	1·00	0·40	0·20	0·110

No. 1 was pig-iron especially selected, containing an abnormal quantity of Sulphur, to show how completely it could be removed, but the other pig-irons, considering the low percentage of Silicon and Manganese, are fairly typical of common iron, and in each case the Sulphur removal is very complete. It may seem doubtful if it is not better and cheaper to make a proper basic pig-iron low in Sulphur by addition of Manganese ores, &c., in the blast furnace, rather than throw the responsibility of removing this objectionable constituent upon the steel maker, and in the author's opinion this is the correct thing to do. But even then there will always be some iron made with high content of Sulphur, and in such cases, or where the local conditions are such that a low Silicon and low Sulphur iron cannot be made economically in the blast furnace, the Saniter process comes to the rescue, and enables high-class steel to be made when it would otherwise be impossible. In cases, too, where fuel for gas production is of inferior quality, so that the metal in the Siemens furnace is liable to take up Sulphur during the process of manufacture, the addition of comparatively small amounts of Calcium Chloride would probably greatly reduce this liability of the metal to absorb Sulphur, if it did not altogether prevent it. The process is not of course applicable for working in an acid-lined furnace, as a slag containing over 50 per cent. of lime is essential; but hematite pig-iron for acid work can of course be desulphurised in the ladle before charging into the furnace. It has been urged against the process that anything like the complete removal of the Sulphur—*i.e.*, to ·03 per cent. or less—greatly increases the length of time required to work a charge of steel, and so reduces the output, and there is certainly some truth in this, although this will greatly depend upon the quantity of Calcium Chloride mixture added, and if this is added in sufficient quantity to maintain a *strongly basic fluid slag* to the end of the operation, the delay in working should not be a serious objection. One curious effect of the Calcium Chloride and Fluorspar appears to be that they considerably reduce the solubility in citric acid of the Phosphoric acid in the slag, an important point, as the value of the slag as a fertiliser depends largely upon this solubility.

Mr. W. G. Burman * has investigated this question by adding varying quantities of Fluorspar (from 1 to 10 cwts.) to the slag in 18-ton steel charges, and the following table gives the results obtained as regards the solubility of the Phosphoric acid with and without Fluorspar:—

TABLE XXXIV.

With the Addition of Fluorspar.				Without Fluorspar.		
Amount of Fluorspar used.	Total Phosphoric Acid.	Soluble Phosphoric Acid.	Solubility.	Total Phosphoric Acid.	Soluble Phosphoric Acid.	Solubility.
Cwts.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
2	17·66	7·42	42·0	15·72	13·3	84·6
7	15·37	2·56	16·6	14·93	13·18	88·2
1½	15·81	8·44	53·3	15·75	14·30	90·8
6	15·81	3·45	21·8	17·07	13·33	83·9
10	13·43	0·78	5·8	16·26	14·12	86·8
5	15·84	3·82	24·1	15·75	13·43	85·2

Hematite and Low Phosphorus Pig-Iron.—In this country most of our Phosphoric ores contain a somewhat high percentage of Phosphorus, and consequently comparatively little or no pig-iron is produced with Phosphorus just outside the hematite limit—say, from 0·100 to 0·500—and our basic steel makers have generally to deal with pig-iron containing at least 1·5 per cent. of Phosphorus, and frequently more. Unless they are prepared to pay an extra price, they have also to take fairly high Silicon. In some parts of the Continent, and in America, where low Phosphoric ores exist and pig-iron with about 0·25 per cent. of Phosphorus is obtainable, the task of the steel maker is a comparatively easy one, as dephosphorisation is

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* *Iron and Steel Inst. Journ.*, 1892, vol. ii., p. 260.

† Supplied by Mr. Saniter.

* *Iron and Coal Trades Review*, January 9, 1903, p. 94.

practically always complete *long before the bath is decarburised*, so that there is really no danger of any appreciable amount of Phosphorus being left in the steel when the final Carbon has been removed, and a very regular low phosphorus steel is the result.

One direction in which the basic process has developed to a small extent when an exceptionally pure material is required for electrical and other purposes is the working of hematite pig-iron charges in the basic Siemens. As it is difficult to get English hematite iron low in Silicon without being high in Sulphur, and as high Silicon pig causes endless trouble in a basic furnace, it is not only advisable, but practically necessary, to use what may be termed a basic hematite—that is to say, a pig made from hematite ores with Manganese ores added, so that the pig-iron is low in Silicon and Sulphur and contains about 2 per cent. of Manganese. Considering how easily such pig-iron is treated in the basic furnace, the small extra cost of working the process compared with the acid, and the extraordinary purity and regularity of the final product, it is somewhat surprising that more acid steel makers have not put basic linings into their furnaces to treat pig-iron of this description, and made special arrangements with the blast furnace people for the production of a suitable pig-iron. Below are given the analyses of samples taken from a hematite charge during every half-hour, and they show very clearly that almost directly the bath is melted the Phosphorus is reduced below the average of that present in high-class acid steel in the finished state.

TABLE XXXV.—CHEMICAL ANALYSES OF STEEL SAMPLES TAKEN AT INTERVALS OF 30 MINUTES, DURING THE WORKING OF A HEMATITE CHARGE, IN A BASIC SIEMENS FURNACE PRODUCING LOW CARBON STEEL.

Nos.	Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Arsenic.
1	1·800	0·008	0·032	0·054	0·391	trace
2*	...	...	...	...	...	...
3	1·740	0·006	0·037	0·046	0·380	trace
4	1·451	0·006	0·029	0·023	0·340	0·004
5	1·461	0·007	0·038	0·025	0·340	0·002
6	1·234	trace	0·030	0·013	0·327	0·004
7	1·161	,,	0·030	0·016	0·290	trace
8	0·927	,,	0·025	0·013	0·293	0·004
9	0·912	,,	0·036	0·010	0·236	trace
10	0·871	,,	0·040	0·008	0·270	0·002
11	0·690	,,	0·038	0·009	0·220	0·004
12	0·540	,,	0·032	0·006	0·280	trace
13	0·434	,,	0·030	0·009	0·270	,,
14	0·342	,,	0·032	0·006	0·270	0·003
15	0·160	,,	0·037	0·008	0·240	trace
16	0·145	,,	0·041	0·006	0·250	,,
17	0·102	,,	0·037	0·008	0·230	,,
18*	...	...	...	...	...	...
19	0·070	trace	0·035	0·008	0·244	trace
20*	...	...	...	...	...	...
21	0·097	trace	0·030	0·007	0·220	0·004
22*	...	...	...	...	...	...
23	0·108	trace	0·033	0·005	0·240	trace
24	0·101	,,	0·034	0·004	0·217	,,
25	0·078	,,	0·033	0·007	0·217	,,

* Nos. 2, 18, 20, and 22 were not analysed.

The samples were kindly supplied by Mr. Darby, of Brymbo, for the late Sir Wm. Roberts-Austen's experiments, in connection with the Alloys Research Committee, and the analyses were made by the author. In view of the fact that our own hematite ores are rapidly becoming exhausted, and that many of the large Spanish deposits are also, to a very large extent, being depleted, it is a question worthy of the serious consideration of our iron and steel manufacturers, whether it would not pay better to make a basic pig from part hematite and part native ores, to contain, say, not more than 0·50 per cent. of Phosphorus, and to work such pig in basic furnaces in preference to hematite pig by the acid process. There can be no reasonable doubt that starting with such a low Phosphoric pig-iron, a steel could be produced which, both as regards regularity of chemical composition and mechanical properties, could hold its own for all structural purposes with any steel produced in the world.

As things are at present, however, it is often difficult to obtain such pig-iron fairly low in Phosphorus, and low in Silicon and Sulphur, although there is no difficulty in obtaining *high* Silicon pig low in Sulphur. To meet this difficulty many attempts have been made at preliminary refining previous to treatment in the basic Siemens, some proposals being to simply desiliconise, and others to both desiliconise and dephosphorise.

The simplest way of desiliconising is to blow the molten metal from the blast furnace for a few minutes, generally about six minutes, in an acid-lined Bessemer converter, and then transfer in the molten state to an open hearth or Siemens furnace to dephosphorise and decarburise. This method of working is practised in some German works, but the waste in Bessemerising and cost of maintaining two plants has prevented its being at all generally adopted. At some works with which the author was connected some years ago, experiments were made in this direction, but after trials extending over a considerable time, they were abandoned, as it was found cheaper to pay a higher price for specially-selected pig-iron.

The processes which seem to offer the best promise of success are some modifications of the washing process of Sir Lowthian Bell, by which the iron can be largely desiliconised, and also, to a considerable extent, dephosphorised, by the action of an oxidising slag at a comparatively low temperature without appreciably removing the Carbon.

Production of Pure Iron in Basic Open Hearth from Phosphoric Iron.—Until comparatively recently it has been generally held that the addition of manganese to steel made in the open hearth process was absolutely essential to obtain a satisfactory product, and steel which contained less than ·15 per cent. of Manganese would be red short and incapable of being rolled or forged. For several years past a product has been made in the United States and is now being produced in this country in the basic open hearth furnace which contains 99·80 per cent. of iron. The charge is worked down in the usual way with limestone or lime and ore until the Carbon is below 0·1 per cent. and Phosphorus and Sulphur below 0·04 per cent.; the refining process is then continued at a high temperature for about one hour longer, further additions of ore being made until Manganese and Carbon are reduced to about ·02 per cent. During this refining the bath of metal becomes over-oxidised, and comparatively large quantities of Aluminium, equal to about 1 to 1½ lbs. per ton, are added to the charge in the ladle. By this means the metal is deoxidised and degasified to such an extent that ingots containing not more than 0·05 per cent. of oxygen are obtained. It is claimed by the patentees that any deoxidising agents except Carbon and Manganese can be used and similar results obtained.

The material is capable of being rolled into thin sheets, bars, etc., without showing any signs of red-shortness at certain temperatures, but there is a range of temperature within which the metal is so red-short that it cannot be rolled. This critical or red-short range of temperature, according to Dr. Stead, coincides with the Ar_3 range, and practically it is advisable to roll at a temperature above 950° C., or to stop rolling when the temperature of the material falls to 950° C., and allow it to cool to 850° C., when it can be again rolled without any signs of red-shortness. The analysis, kindly supplied by Dr. Stead, varies between the following limits. It is being sold under the trade name of Armco Iron :—

C, ...	0·02 per cent. to	0·03 per cent.
Mn, ...	0·05 ,,	0·07 ,,
Si, ...	nil ,,	nil ,,
S, ...	0·01 ,,	0·02 ,,
P, ...	0·008 ,,	0·010 ,,
O, ...	0·020 ,,	0·050 ,,

This very pure material is equal to purest Swedish bars, and experiments for the production of high-class crucible steel from it are being made by Dr. Stead.

A somewhat similar material, but not quite so pure, is being made without any addition of Aluminium, or at all events without more than a few ounces per ton being added, as is frequently done when making ordinary steel. In this case, after over-oxidising the steel, it is necessary to remove as far as possible the oxidising slag and make a new slag as neutral as possible by lime additions, and to hold the metal in the furnace for a considerable time, some pig-iron being added before tapping to deoxidise the bath. In this way metal containing not more than ·3 to ·35 total impurities, including Carbon and Manganese, is obtained. Both these pure materials have very low electric resistance, and probably will be largely used in the future for the conducting rails for electric railways and similar purposes. It is also claimed that the very pure iron resists corrosion to a remarkable extent compared with ordinary steel. The material, made with little or no Aluminium, containing slightly more impurities than the material made with excess of Aluminium, can only be rolled within the same range of temperature, and to obtain a steel which can be forged and rolled at all temperatures from a low red to a welding temperature, it is necessary to add Manganese as usual to the molten steel.

The Talbot Washing Process.—In 1892, Mr. Benjamin Talbot introduced a new washing process for the treatment of the very silicious irons of Alabama, which consisted in running the pig-iron from blast furnace, cupola or mixer through a bath of molten basic slag, obtained from an open hearth furnace. The slag (from an open hearth furnace) was run into a basic-lined vessel, and molten iron was poured in a thin stream through this, and after being allowed to stand for a short time was either taken in the molten condition to an open hearth furnace or cast into moulds, and then charged into the furnace in the solid state. The slag from a finished heat of steel was found to be sufficiently oxidising to remove the Silicon and also part of the Phosphorus, and the heat developed by the chemical reactions was sufficient to maintain the metal in a fluid condition. If further oxidation was required, fluid Oxides or finely-divided solid Oxides were run into the containing vessel with the slag. Very excellent results were obtained by this process, but owing to the readiness with which low Silicon, Sulphur, and Phosphorus iron can be obtained in the States, it has not been used to any extent.

Krupp's Dephosphorising Process.—Another process depending upon the removal of impurities by fluid Oxides, is the Krupp washing process, which consists in running molten iron from a cupola into an open hearth furnace, the hearth of which is inclined and revolves, and in fact is somewhat similar to the old Pernot furnace. The hearth of the furnace is lined with red ore by packing in small and large lumps, and thoroughly glazing the whole by heat. This hearth section is on a carriage, and can be removed when required. It is revolved by a steam engine, three or four times per minute, during heating up, and when the hearth is ready 700 to 800 lbs. of ore are charged and well heated. With very Phosphoric pig-iron more ore is added up to, say, 1,000 lbs., and if the iron is silicious some lime additions are made.

When the ore is raised to a white heat, melted pig-iron is run from the cupola, and the hearth rotated at a rate of about 10 or 11 revolutions per minute. After two or three minutes a vigorous reaction takes place, which lasts for about two minutes, when the bath becomes quieter, and the Carbonic Oxide begins to escape. If it is wished *not* to decarburise, the metal must be tapped at once, but if it is desired to carry dephosphorisation further, a little Carbon will necessarily be removed during the process. The whole operation up to the beginning of the evolution of CO gas lasts five minutes, and for the more complete dephosphorisation eight to ten minutes, the tapping taking a further three minutes. The dephosphorised metal is then transferred to an ordinary open hearth furnace, in which three heats can be made in twenty-four hours, using the dephosphorised metal without scrap.

The pig-iron should contain about 1·0 per cent. Manganese, not above 1·0 per cent. Silicon, and should be as high as possible in Carbon. The following are several analyses of metal samples taken before and after the dephosphorising, by which it will be seen that Carbon is not appreciably removed :—

		Before Treatment.	After Treatment.
1.	Carbon, ...	3·990	3·75
	Phosphorus, ...	0·632	0·132
2.	Carbon, ...	3·810	3·560
	Phosphorus, ...	0·450	0·108
3.	Carbon, ...	3·170	3·020
	Phosphorus, ...	1·220	0·300

The Carbon, after treatment, is all combined, and the fracture of the refined iron is white.

This process has been worked more or less as a secret process, and very little is known as to the yield, output, and costs of manufacture; but there seems no reason why a preparatory furnace on this principle without any revolving hearth, but worked at a low temperature to dephosphorise and desiliconise, should not play an important part in the future of the basic Siemens process, especially when dealing with very Phosphoric and irregular irons; although, of course, it would be better to do the whole operation in one furnace if possible, if equal rapidity of production and regularity of product could be ensured. In America a very pure material is obtained by treating hematite iron by this or a similar process, and the so-called " washed iron " is largely imported into this country and used to replace Swedish irons when very pure metal is required. Two analyses gave the following results :—

Carbon, ...	3·05	3·00
Silicon, ...	0·0097	0·010
Sulphur, ...	0·0027	0·0065
Phosphorus, ...	0·0077	0·0085
Manganese, ...	0·147	trace.