UNITED STATES PATENT OFFICE.

JAMES HENDERSON, OF BELLEFONTE, PENNSYLVANIA.

PROCESS OF DEPHOSPHORIZING IRON BY MEANS OF FLUORINE.

SPECIFICATION forming part of Letters Patent No. 347,349, dated August 17, 1886.

Application filed June 2, 1885. Serial No. 167,415. (No specimens.)

To all whom it may concern:

Be it known that I, JAMES HENDERSON, of Bellefonte, county of Centre and State of Pennsylvania, (formerly of New York city,) have invented a new and useful Improvement in the Process of Dephosphorizing Iron by Means of Fluorine and Condensing the Gaseous Products Therefrom, of which the following is a full, clear, and exact description.

The object of one part of this invention is to recover from iron containing phosphorus the phosphorus practically free from gelatinous silica; and my invention consists, mainly, in treating the desiliconized molten iron with a compound of fluorine and condensing the phosphorus, as hereinafter described, and recited in the claims at the close of this specification.

The object of another part of the invention is to depurate crude iron of silicon and phosphorus by a continuous operation without removing phosphoric slags from the molten dephosphorized iron before treating it with ferro-manganese or other similar material.

In carrying out this invention I operate upon either crude iron containing silicon or crude iron which has been freed of that material.

As the crude irons generally found in the market almost universally contain silicon, I will first describe the application of my invention to such irons, and the invention in that case comprises two operations—viz., first, the desiliconization of the crude iron, and, second, the removal of the phosphorus and its recovery. The first of these two operations may be performed in the well-known Bessemer converter, and the second operation may be performed in an open-hearth furnace which is fitted with condensing apparatus, as described in Letters Patent granted to me the 14th day of August, 1883, No. 283,342, or any other suitable condenser than that described in the said patent may be employed.

The preferred mode of operating the process is to line the converter and the hearth of the furnace with some suitable basic material, such as lime or magnesian lime, and to charge the crude iron in a melted state direct from the blast-furnace into the converter; but the crude iron may be remelted in a cupola and poured into the converter. The melted iron in the converter is blown in the usual way with air as practiced in the Bessemer process, with or without the use of solid or fluid reagents containing or capable of evolving oxygen. The operation is continued until desiliconization takes place, which is indicated by the color of the flame, as is well understood in the Bessemer process. This desiliconization constitutes the first operation. When it is effected the converter is turned down, and the slag is removed from the surface of the iron. As it may happen that some small portion of silicon may remain in the metal, which portion will be deleterous to the second operation, it is expedient to remove any traces of silicon which may remain in the metal after it appears to have been desiliconized, as indicated by the character of the flame from the converter. This removal may be effected by charging quicklime upon the metal in the converter and blowing the metal for about three minutes, after which the converter should be turned down and the slag removed. The quantity of quicklime which it is expedient to use for this purpose is about thirty pounds for each ton of metal in the converter.

The molten desiliconized iron is now ready for the second operation. For this purpose it is run from the converter into the converting-hearth of the open-hearth furnace, and is therein treated with a compound of fluorine capable of evolving fluorine in the furnace. The compound of fluorine may be fluor-spar or other suitable solid fluoride which may be thrown into the furnace upon the metal, the condition in which the fluoride is charged being in lumps of one to three cubic inches area. In order that the fluorine may be set free from the fluor-spar, an oxidizing reagent is employed, and this reagent may be oxide of iron practically free of silica and sulphur—such, for example, as specular iron ore. The fluoride used should be such as to furnish forty pounds of fluorine to each one per cent. of phosphorous contained in one ton of crude iron, more or less fluoride being used according to the greater or less quantity of phosphorus in the crude iron. The quantity of oxide of iron employed should be about two and one-half times greater than the fluoride. By the action of the heat and the fluorine the phosphorus is vaporized and passes off from the hearth with the products of combustion, and is condensed in the condenser. The operation is continued until the iron is nearly or wholly decarbonized, according to the quality of metal which it is desired to produce, and it is expedient to add ferro-manganese to the molten metal during the process or at the end of the process, for the purpose of removing any oxide of iron or oxygen that may be mixed with the molten metal, the ferro-manganese being applied in the same manner and in the same quantity as is practiced in the manufacture of steel or homogeneous iron in the open-hearth process. Desiliconized cast-iron may, if necessary, be added during the dephosphorizing to maintain the liquidity of the metal. The molten metal is tapped from the furnace and is cast into ingots in the usual manner. The condensers are arranged to cool the gases below the point at 60° Fahrenheit, at which hydrofluoric acid volatilizes. The condensation of the gases produces water, hydrofluoric acid, and phosphorus, and the phosphorus is separated from the other products by draining off the liquid. Milk-lime may be added to the liquid products, in which case a solid fluoride of calcium is produced, which may be dried and used subsequently as the compound of fluorine to be supplied to the iron in the furnace.

In place of using a converter for the first operation and an open-hearth furnace for the second operation, as above described, both operations may be performed successively in a converter, or both may be performed successively in an open-hearth furnace. When both are successively performed in a converter: In this case the latter must be combined with a condensing apparatus, such as is described in my aforesaid patent of August 14, 1883, or the converter must be employed in connection with some other suitable condensing apparatus. When a converter is thus employed, the first operation is conducted as before described, and after the slag is removed the fluorine compound may be introduced during the second operation. In this case the compound of fluorine may be the vapor of hydrofluoric acid, which is decomposed by the heat of the converter, and by its decomposition furnishes fluorine and hydrogen. For this purpose commercial hydrofluoric acid may be used, which consists of about one-third anhydrous acid to two-thirds of water, by weight. This commercial acid is charged into a vessel lined with lead, and is heated so as to become vapor, and it is then forced by an air-pump into the air, which is conveyed in the blast-pipe to the tuyeres of the converter. The air and hydrofluoric vapor pass into the converter. The hydrofluoric acid is decomposed and its fluorine causes the liberation of the phosphorus present in the iron. The phosphorus passes off with the products of combustion to the condenser and is condensed therein, as previously described. In thus performing the second operation in the converter the air which is introduced through the tuyeres supplies a sufficient quantity of oxygen to cause the decomposition of the compound of fluorine, and the use of a solid oxide is unnecessary.

Instead of using commercial hydrofluoric acid or the compound of fluorine, the hydrofluoric acid which is received in the condenser may be used for the purpose, the quantity used for each charge of metal being proportioned to the strength of the acid, so as to supply about forty pounds of fluorine to each one per cent. of phosphorus contained in one ton of crude iron, as previously described.

The air and the hydrofluoric vapor may be introduced separately into the iron in the converter through separate tuyeres, but the two should be introduced simultaneously.

I prefer to apply the hydrofluoric acid in a measured proportion to the quantity of air used, which proportion may be obtained by regulating the speed of the air-pump, which forces the acid vapor to the speed of the blast-engine which supplies the air, the speed of the acid-air pump being so regulated that it supplies the requisite amount of acid vapor to furnish about forty pounds of fluorine for each one per cent. of phosphorus contained in a ton of iron in the converter during the time required for the decarbonization of the iron by the action of the air-blast.

Instead of using the vapor of hydrofluoric acid as the compound of fluorine, fluor-spar may be used. This latter compound may be thrown into the converter in lumps, or may be powdered and blown in with the blast through the tuyeres. During the second operation in the converter the blast must be kept up, in order to maintain the heat of the metal.

When both operations are to be conducted successively in the same open-hearth furnace, the hearth should be fitted with a tap-hole at a suitable height for drawing off the slag from the molten metal at the end of the first operation before the metal is treated with the compound of fluorine; or the hearth may be lowered and tapped for the purpose of discharging the slag at the close of the first operation, after which the hearth may be raised for the second operation. The desiliconization is effected by the use of oxide of iron in the form of iron ore as free as practicable from sulphur, phosphorus, and silica, the iron ore being thrown into the furnace on top of the iron in lumps of from one to three cubic inches area, and in the proportion of about six hundred weight of iron ore for each ton of iron in the furnace. The use of iron ore effects both the desiliconization and decarbonization of the iron, and the operation is continued until the iron becomes decarbonized, as indicated by samples removed from the furnace. Then the slag is removed from the iron, and the desiliconized metal is treated with the compound of fluorine, as above described, for the second operation.

When the second operation is conducted with desiliconized metal, as above described, the removal of the phosphorus from the iron takes place during the decarbonization of the latter; but I do not limit my invention to removal of the phosphorus during decarbonization, as the metal may be decarbonized by means of solid oxidizing reagents, as above described, or by the action of jets of air, and the metal thus decarbonized may then be treated with the compound of fluorine, as above described, whatever slag which has been produced during the decarbonization being removed before the decarbonized metal is treated with the compound of fluorine.

Thus far I have described the desiliconization of the iron and the subsequent treatment of the desiliconized metal with the compound of fluorine, accompanied with the condensation of the phosphorus; but one portion of my invention is not restricted to the desiliconization of the iron, it being evident that iron which has been previously desiliconized, or iron which is practically free of silicon in its natural condition, may be melted and treated with the compound of fluorine for the removal of phosphorus; and the phosphorus may be recovered by condensation, as previously described.

Instead of charging the fluor-spar and oxide of iron (or other solid oxidizing reagent) separately, the two may be powdered and formed into lumps or small bricks, which are thrown into the furnace; and in case the flame employed to heat the open-hearth furnace during the second operation is sufficiently oxidizing to liberate the fluorine from the fluoride, the use of a solid oxidizing reagent is not essential. In every case the crude iron which is used should be practically free of sulphur, for if an iron containing sulphur be used the hydrofluoric acid which is condensed during the process is mixed with sulphuric acid; besides, if sulphur be present in the iron under treatment, I have found it expedient to increase the amount of fluorine, supplied in the proportion of forty pounds of fluorine for each one per cent. of sulphur contained in the metal, as I have found that the sulphur combines with the fluorine, and if the quantity of fluorine is not increased there is not enough of it to effect the removal of the phosphorus.

The process above described not only depurates the iron of phosphorus, but enables the phosphorus to be recovered as a by-product, the phosphorus being free of gelatinous silica or hydrofluo-silicic acid. When the crude iron is free from sulphur hydrofluoric acid is also obtained as a by-product.

By the process above described the phosphorus is separated from the desiliconized iron almost wholly in the condition of gas or vapor, and consequently the slag formed during dephosphorization contains so little phosphorus that it does not recombine with the iron when ferro-manganese or cast-iron is added at the close of the dephosphorization, and therefore the slag which is formed during decarbonization need not be removed prior to such addition.

I do not wish to be understood as limiting my invention to the converter or furnace herein described, as the processes may be practiced in a refining-fire connected with a condenser; or other suitable furnace and condenser may be employed.

In previous patents granted to me June 26, 1883, No. 279,947, and August 14, 1883, No. 283,342, I have described the depuration of silicious phosphoric iron of phosphorus and silicon simultaneously by the use of fluorine; but in those cases the phosphorus recovered is mixed with gelatinous silica, and whatever hydrofluoric acid is recovered is mixed with hydrofluo-silicic acid, which greatly depreciates its value for some purposes. The present invention is distinguished from that of the said previous patents by the fact that the phosphoric iron to be treated must either be iron free of silicon, or, if containing that substance, must be desiliconized before the phosphorus is separated from it, the silicon and phosphorus being separated from the iron separately and consecutively, instead of simultaneously, as previously; nor do I wish to be understood as now claiming subjecting molten iron in a suitable chamber lined with a basic or non-silicious material to jets of air to desiliconize it, and pouring the silicious slags from the chamber, and afterward treating the desiliconized metal with jets or blasts of air and steam to remove the phosphorus, as this is described in Patent No. 283,783, dated August 28, 1883, already granted to me.

What I claim as my invention, and desire to secure by Letters Patent, is—

1. The process, substantially as before described, of depurating desiliconized crude iron of phosphorus and recovering the phosphorus by treating the molten iron with a compound of fluorine and condensing the gaseous products of the treatment.

2. The process, substantially as before described, of depurating crude-iron of phosphorus and recovering the phosphorus by first desiliconizing the crude-iron, and then treating the molten desiliconized iron with a compound of fluorine and condensing the gaseous products of the treatment.

JAMES HENDERSON.

Witnesses:

JOSEPH J. SULLIVAN,
JOHN E. ELMENDORF.