

UNITED STATES PATENT OFFICE.

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PROCESS OF MANUFACTURING MANGANESE METAL.

SPECIFICATION forming part of Letters Patent No. 556,457, dated March 17, 1896.

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To all whom it may concern:

Be it known that we, JOHN W. CABOT, residing at Johnstown, and SAMUEL W. VAUGHEN, residing at Coopersdale, in the county of Cambria and State of Pennsylvania, citizens of the United States, have invented certain new and useful Improvements in Processes of Manufacturing Manganiferous Metal; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

In the Bessemer or pneumatic process of making steel, molten pig-iron is "blown" in a converter until it comes to the chemical condition of wrought-iron. To this molten mass is added certain proportions of a metal called "spiegeleisen" which is a compound of iron, manganese, carbon, and silicon. This changes the melted wrought-iron into steel. The carbon confers the desired hardness to the steel, the manganese the quality of malleability. The desired carbon may be obtained in other ways; but the manganese, which is a necessity in the process, has heretofore been obtained only by the use of this spiegeleisen which is a costly metal to manufacture. It is customary in its manufacture to use certain mixtures of expensive manganiferous ores, carrying from ten per cent. to fifty per cent. of manganese. To such mixtures are added limestone to flux the earthy impurities of the ores and fuel, usually either coke or coal, and the whole is commonly smelted in a blast-furnace. This produces a metal known as "spiegeleisen" in which manganese runs from eight per cent. upward, having carbon from four to six per cent. and silicon up to three per cent., the remainder being iron. The kind most commonly used, however, contains ten per cent. to eighteen per cent. manganese. In the manufacture of this grade of spiegeleisen these ores, fluxes and fuels are so mixed and proportioned that the percentage of the element iron in the mixture shall bear a certain fixed ratio to that of the element manganese, allowing for the unavoidable loss of some manganese, which goes into the waste slag in the smelting operation. This relation of iron to manganese is that of about three (3) of iron to one (1) of manganese. If this ratio is

not maintained the resulting spiegeleisen will not be of the grade that is desired. The ores used are difficult to obtain cheaply, and exist in but a few places and always in uncertain quantities. For this reason they command high prices. Manganese being a necessary constituent of steel made by the Bessemer as well as by the open-hearth process, and the consumption of it increasing for these purposes every year with the expansion of the world's production of steel, the fact of the limited supply of its ores has made the problem of the future supply of this metal a difficult one, and the problem is practically narrowed down to that of the metal manganese, because the other elements of the spiegeleisen may be obtained in a variety of ways. As under present methods the supply of manganese is liable to be exhausted, it is imperative that some other different source should be found. All or nearly all pig-irons used in the Bessemer process contain small amounts of manganese from, 0.25 per cent. to 2.50 per cent; and our improvement consists in a new and improved process of collecting and saving this manganese and in manufacturing it into a metal similar to spiegeleisen, and is carried out in the following way:

The manganese which is contained in the pig-iron to be treated by the Bessemer process becomes changed to oxide of manganese during the course of the "blowing" operation and is absorbed in the slag or cinder produced in the operation and is poured off separately from the blown metal at the end of the operation. This slag or cinder has heretofore been regarded as a waste product. It contains, in addition to the above-mentioned oxide of manganese, about thirty per cent. of iron, small amounts of other elements, and all of the silicon contents of the pig-iron operated upon in the form of the oxide of silicon or silica, also large quantities of silica from the wearing of the silicious lining of the converter, some of which is free silica and some exists as silicate of manganese and iron. In these forms it is present in great excess, and in such excess is a very injurious element in ordinary blast-furnace operations. Many thousands of tons of slag containing it have been and are still being thrown out on

the waste-heaps. We have discovered that in this material, excepting the excess of silicon, the elements exist in such ratios to each other that it is very suitable for the manufacture of a manganiferous metal which will serve the same purpose which spiegeleisen has done heretofore, and that by its use the manufacture of steel will not be as at present wholly dependent upon the use of manganiferous ores of rare occurrence in the making of the spiegeleisen necessary in the operation.

We have found by analysis and by theoretical deductions, and by practical experiments upon a manufacturing scale, that this manganese contained in small quantities in ordinary Bessemer pig-iron and which in the very act of conversion becomes nearly all concentrated in the waste slag may by our treatment be separated from its excessive contaminating silica and in alloy with the iron, and small amounts of other elements may be recovered in the form of a metal suitable in all ways to be used like spiegeleisen in conferring to blown Bessemer metal the necessary amount of manganese (also carbon) to make it into steel. It is the presence of this excessive quantity of silicious impurity in the converter waste slag which has heretofore prevented its use in the manufacture of ordinary pig-iron, and until our discovery was made it was not known that it could be used in the way that we do use it—that is, for making this new kind of metal. If used as in the ordinary practice of making spiegeleisen with the quantities of fuel and flux heretofore found necessary, the large amount of its silica would in smelting carry off nearly all of the manganese originally present in the charge in the form of silicate of manganese in the slag, for the reason that it would produce nearly three times as much volume of slag as would be the case when using ordinary manganese ores.

In the manufacture of spiegel in the usual way it has been found difficult to reduce the loss of manganese in the slag below eight per cent. This percentage figured on three times the amount of slag would carry off nearly all of the manganese put in with the charge. Such excessive loss of the manganese in the furnace-charge of converter-slag we prevent by our method of treatment. To its excessive silica and silicate of manganese we add an excess of lime, which we have found will, under proper temperature conditions in a blast or reducing furnace, form a chemical union with the silica of the silicate of manganese in the slag, forming a silicate of lime, thus displacing the manganese from its combination and leaving it free in the metallic state. In order to effect this chemical interchange between the manganese and the calcium, there must be a high temperature in the hearth of the reducing-furnace, which we effect by the

use of a correspondingly excessive quantity of coke. By this method of treatment we have discovered that the amount of loss of manganese in the slag may be reduced to less than one-half of that obtained in any ordinary blast-furnace practice, and the manganese may be forced out of combination with the silica and recovered as a useful product. This treatment also reduces nearly all of the iron present in the converter-slag and some silica. By a proper regulation of the temperature conditions and the chemical condition of the slag and by making up the furnace charge in certain proportions we have found that the relative proportion of iron and manganese reduced from the mixture and collected at the bottom of the furnace will give a manganiferous metal having the desired balance between iron and manganese, and which we have used successfully in place of spiegeleisen.

In the ordinary blast-furnaces in the manufacture of iron there is used about one-fourth of a ton of limestone to a ton of ore and about one-half ton of coke to a ton of ore; but to work our process most effectively it is necessary to use a ton of limestone to a ton of the waste slag and three-fourths of a ton of coke to a ton of slag. Less than six-tenths of a ton, respectively, of limestone and of coke to a ton of slag in the charge will not be found effective.

We prefer coke for the charge, but do not limit ourselves to it, as an equivalent amount of coal or other fuel can be used.

The mixture which we have given above is that which we prefer in practice for producing manganiferous metals suitable for use in the Bessemer process, and the reduction of this charge in an ordinary blast-furnace or other furnace makes a manganiferous metal containing from eight per cent. to twenty-five or more per cent. of manganese.

Having thus fully described our invention, what we claim, and desire to secure by Letters Patent, is—

The process of manufacturing a manganiferous metal by introducing into a blast or other furnace a charge consisting of slag from Bessemer converters, mixed with coke and limestone in the proportions of not less than sixty pounds of coke and sixty pounds of limestone to each one hundred pounds of slag, and reducing the same, substantially as described.

In testimony whereof we affix our signatures in presence of two witnesses.

JOHN W. CABOT.
SAMUEL W. VAUGHNEN.

Witnesses:

D. J. JONES,
H. C. BEUFORD.