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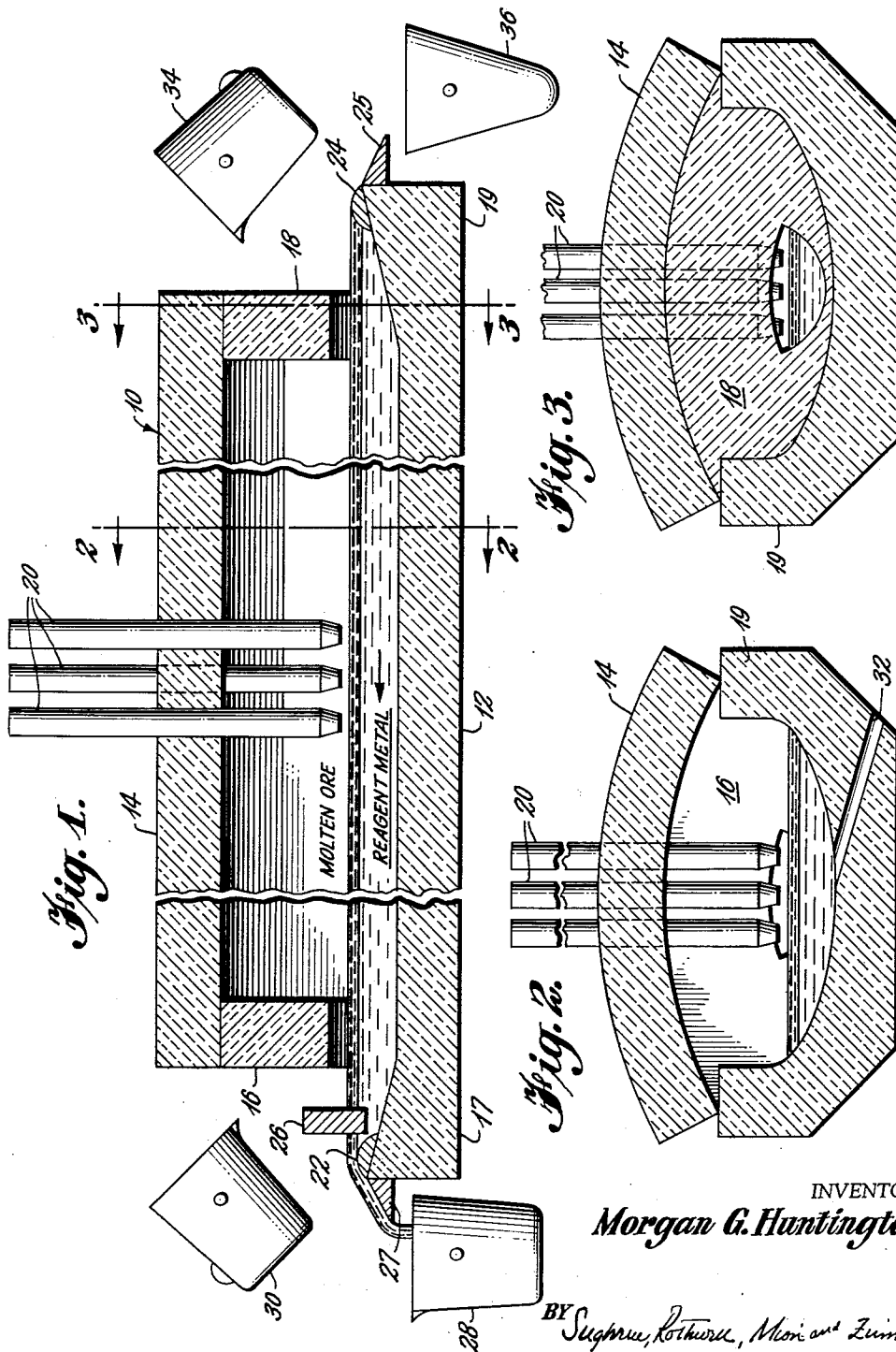
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METHOD FOR CONTINUOUS HEARTH REFINING OF STEEL
AND BENEFICIATION OF ORES OF FERRO ALLOYS

Filed May 21, 1959

3 Sheets-Sheet 1



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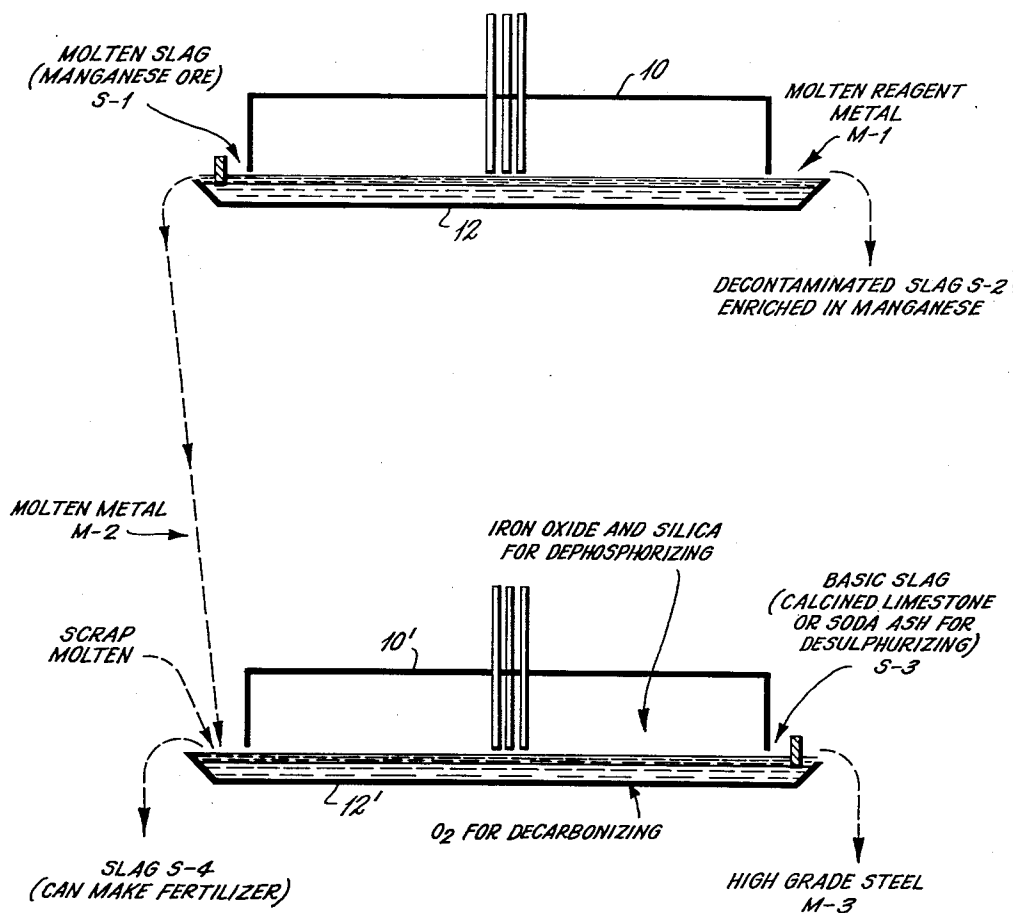
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3 Sheets-Sheet 2

Fig. 4.



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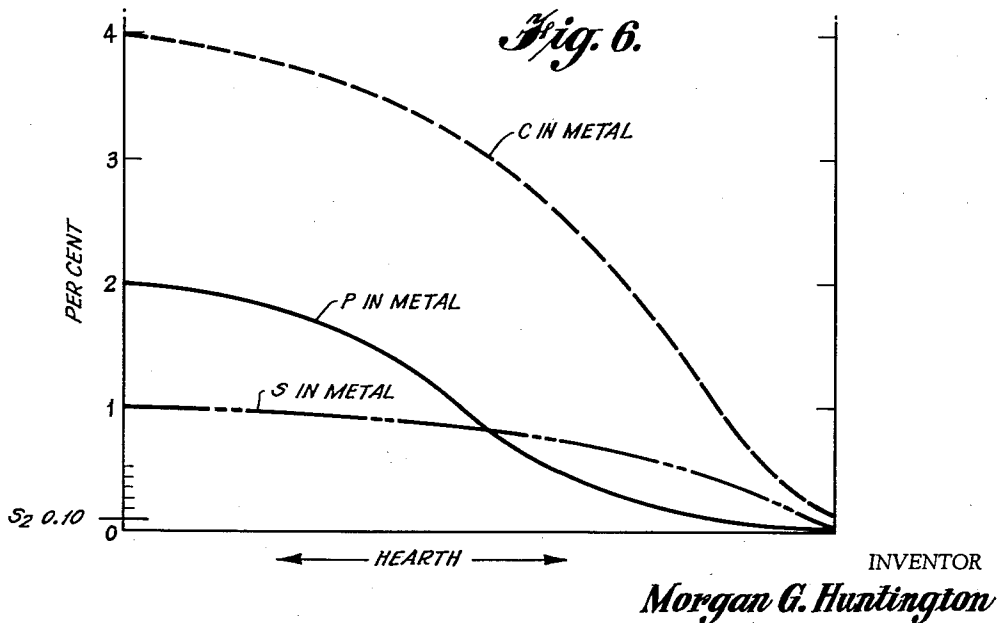
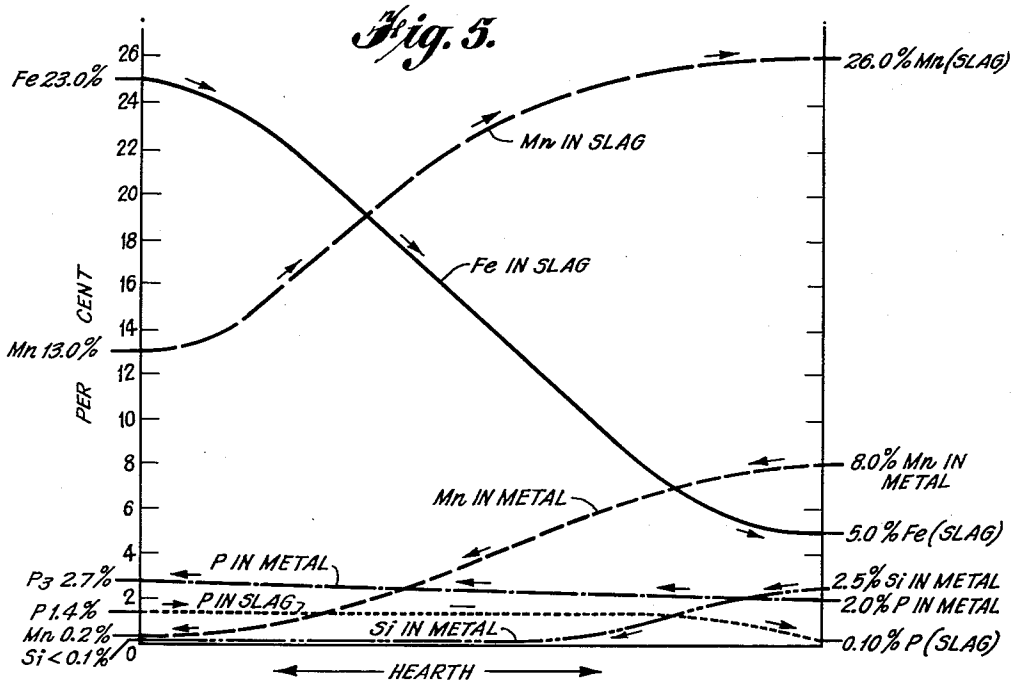
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3 Sheets-Sheet 3



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3,022,157

METHOD FOR CONTINUOUS HEARTH REFINING OF STEEL AND BENEFICIATION OF ORES OF FERRO ALLOYS

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This invention relates to the preferential molal exchange across the interface of molten metals and molten slags and is especially concerned with a method and apparatus for continuous beneficiation and decontamination of molten ores during the refining of ferruginous alloys such as pig iron, spiegeleisen, phospho-spiegeleisen, cupola molten scrap and other ferrous alloys.

This invention particularly relates to the continuous counter flow and preferential molal exchange chemical reaction between molten ore and molten metal in long, shallow, reverberatory furnaces which continuously produce one or more slags.

This invention also relates to method and apparatus for decontaminating and coincidentally enriching molten ores, and particularly relates to the accomplishment of these purposes incidental to my method of refining molten ferruginous alloys into commercial grades of steel.

The refining of ferruginous alloys into commercially acceptable steel is essentially the process of oxidizing the metalloids from the bath into the slag and subsequently adding the required amounts of deoxidizers and ferroalloys just before the ingot molds are filled with molten steel.

In a converter process, the oxidation of the metalloids from the metal bath is accomplished by blowing air or oxygen through or against the molten metal. The open hearth and electric furnace processes accomplished the oxidation of metalloids in three ways; by the addition of oxide ores, by the direct addition of oxygen through oxygen lances, or by an atmosphere rich in oxygen above the bath.

In conventional steel making processes where chemical reactions are predominantly those between slag and metal phases, such as those in the electric furnace and in the open hearth furnace, it is well recognized that stirring and agitating the metallic bath reduces the time required for the finish of the refining process. The effect of stirring is to increase the area of interface between slag and metal. In spite of the various stirring methods which have been proposed and used, the reduction of metalloids proceeds rapidly at the start of these refining processes and more slowly as the slag and metal approach equilibrium in the conventional open hearth and electric furnace processes.

Although the top oxygen blown, basic lined converter is currently popular in the United States, it has many limitations. The amount of scrap which may be added is limited to eleven or twelve percent, and the metallic yield of iron is only about eighty-five percent of that charged into the converter, and as in all converters the final analysis is unpredictable. The problems of controlling the fume nuisance are serious. This type of steel refining process is applicable where there is much more pig iron entering the system than scrap. The installations so far made in this country are in those plants where there are also electric furnaces which operate most economically on remelting scrap.

The open hearth steel refining method which is responsible of some eighty percent of America's steel production is costly in heat, power and time and is wasteful of natural resources. All of the phosphorus is generally wasted as unusable slag, as is three-quarters of the manganese contained in the pig iron and scrap. No attempt is

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made to separate manganese from phosphorus in the open hearth process. In the open hearth process, this waste of natural resources annually amounts to more than a half-million tons of metallic manganese and three quarter-million tons of phosphate fertilizer.

The open hearth steel refining process requires a specific grade of pig iron, known as basic iron, which is nominally less than 1.25 percent of silicon, less than 0.05 percent of sulphur, and less than 0.5 percent of phosphorus and about 2.0 percent of manganese. Heavy melting and bundled steel scrap of specific grades along with circulating mill (home) scrap make up about half the open hearth charge. The open hearth process does not economically refine charges composed of all scrap or all pig iron without the so-called duplexing or preblowing of the hot metal in a converter.

The ideal steel refining process would accomplish the removal of all metalloids in an automatic and continuous manner so that frequent control sampling would be unnecessary, regardless of the amounts of phosphorus, manganese, silicon, or sulphur originally contained in the bath. Further, an ideal process would make use of the existing thermodynamic potential between slag and metal and accomplish this removal of the metalloids through the coincidental reduction of iron oxide from the slag and, thereby, substantially increase the net output of metallic iron.

My method is essentially a continuous flow process, whereas most other steel refining methods are essentially batch processes. While I employed all of the well known open hearth and electric furnace thermochemical reactions which occur between slag and metal across the interface of the two, my invention provides and automatically maintains conditions which accelerate and insure the uniform completion of the desired reactions. Thus, the usual steel refining reactions may be speeded up and plant capacity may be substantially increased while uniformity of product is maintained.

Unlike the conditions within the open hearth and the electric furnace batch processes wherein the slag and metal are nearly at equilibrium during and especially towards the finish of the heats, in my continuous process, slag and metal never approach chemical equilibrium. On the contrary, in my continuous ore decontaminating and enriching and steel refining process, slag and metal flow countercurrently so that the maximum state of chemical imbalance between slag and metal is maintained from the start to the finish of the process. Thus, in my continuous method, the reactions between slag and metal proceed at the maximum rate, and all possible reactions between slag and metal are virtually completed, to the total practical impoverishment of the active constituents of each. Also, because of the counterflow and the maintenance of maximum chemical unbalance, my process is not dependent upon the diffusion rate of the slag and metal. No stirring is necessary and the results are the same or better than if stirring were to be used.

Obviously, if there were but one constituent in the slag and only one reacting constituent in the metal, a batch process would suffice, and slags could be changed from time to time until one constituent was completely removed from the metal and the other had been exchanged from the slag. However, in all batch processes of this nature for steel-making or other pyrometallurgical operations, reactions between slag and metal across the interface of the two begin between the most active of the several constituents, and, until the most active is completely spent, not much else happens. For instance, if one were to put a slag of iron oxide and iron phosphate into a heated vessel and pour in a batch of molten pig iron or spiegeleisen containing from one to four percent of silicon, or even more, the reaction between slag and metal

would proceed violently until the silicon was exhausted and the equilibrium between iron oxide and manganese and manganese oxide and iron was established. Very little phosphorus would be reduced from the slag if free iron oxide remained in excess, following the oxidation of all of the silicon. In a batch process, then, the only insurance of removing all of the phosphorus from the slag (or subject ore) is to provide sufficient silicon to reduce all of the iron oxide plus all of the phosphates. The net result thus achieved in a batch selective reduction of phosphorus and iron by silicon is the replacement of little or no iron oxide by manganese oxide and the degradation of the slag or subject ore with iron silicate. Although decontamination of the subject ore of phosphorus and iron is accomplished by the addition of silicon or ferrosilicon, the manganese weight percent is lessened due to the degradation of the subject ore by iron silicate.

In my process, however, since both slag and metal are flowing countercurrently, although either may be stopped while the other flows in order to adjust the analysis, the process is a continuous pyrometallurgical refining process. The slag which flows towards the end at which the metal is poured into the furnace, contains all of its original phosphorus, while it has been impoverished of iron oxide by the molal exchange of manganese for iron. Therefore, the fresh, hot metal being poured into the furnace, which contains silicon, has nothing much to react with except the phosphate slag which it promptly reduces to an iron phosphide. This, then, is my method of preferential molal exchange. In other words my method contemplates exchanging constituents in the slag and metal in a preferential manner, the first exchange occurring at one end of the furnace and paving the way for a second molal exchange occurring toward the other end of the furnace. The second molal exchange referred to above is the first molal exchange of the molten counterflowing slag and it likewise makes the other molal exchange easier by its action.

In the refining of pig iron and similar materials into steel by my multi-function method, at least two slags are preferably produced, one in each step. One of these slags is considered acid and contains practically all the manganese and silicon, and the second is basic and contains practically all the phosphorus and sulphur.

Unlike any other steel refining process, my continuous hearth method is completely flexible in respect to proportions of pig iron and scrap. My process has practically an unlimited tolerance for the metalloids such as sulphur, silicon, phosphorus and manganese. Sulphur pick-up in the melting process is not critical because relatively large amounts of sulphur are removable from the bath, using an additional continuously removed slag, if necessary.

My continuous hearth process is based upon several well-known thermochemical reactions between slag and ferrous metal baths which commonly occur in the open hearth and electric furnace steel refining processes. From these well established practices are deduced the following axioms which form the basis of my continuous hearth method:

Silicon in a molten metal bath can cause practically all of the phosphorus compounds to be reduced from acid slags to the bath as iron phosphide.

Silicon and manganese in the molten bath will cause iron oxide to be reduced to the metallic state and the silicon and manganese from the bath will be oxidized to form manganese silicate in the slag.

In the absence of silicon in the bath, manganese will exchange with iron in iron oxide and/or iron silicate and iron will be reduced to the metallic state and the slag will become coincidentally enriched in manganese oxide.

In the absence of silicon, manganese and carbon, phosphorus is readily oxidized from a metallic bath to form phosphate slag in the presence of calcium oxide and iron oxide.

A slag rich in lime and iron oxide will remove practically all phosphorus from the metallic bath.

A slag rich in lime and deficient in iron oxide will favor the removal of sulphur from the metallic bath.

At present, there is no commercial process for reclaiming manganese from steel plant wastes and/or from low grade ores, since no proposed method has yet been found commercially for one or more of these three reasons; the process is too expensive to operate; the metal recovery is too low to be of economic interest; and no apparatus has been found completely satisfactory as to cost of operation and of maintenance.

Probably the most extensively investigated process for the recovery of manganese from steel plant wastes and from low grade and/or contaminated ores is the pyrometallurgical operation commonly referred to as "Selective Oxidation." The fundamental pyrochemical laws of this process are the facts that the elements silicon, manganese, carbon, phosphorus and iron can be oxidized from the ferrous bath in that order in a basic lined vessel.

The first part of the basic Bessemer converter blow has served in Europe to recover some usable manganese from steel plant wastes. In practice, the blow is interrupted before any appreciable amount of phosphorus has been oxidized; the manganese rich slag is poured off; and the blow is then resumed to complete the decarbonization and the de-phosphorization of the molten metal bath for the production of ingot steel.

Under Dr. Russel C. Buehl, as described in this patent assigned to the United States of America, No. 2,687,952, issued August 31, 1954, the Bureau of Mines has improved the recovery of manganese in the basic converter process by the "Buehl Overlap Step." This selective oxidation involves four separate functions; blowing the metal until all the oxidizable manganese has left the bath and entered the slag as manganese oxide; tapping the blown metal from beneath the converter slag (so-called vessel cinder); pouring a fresh, hot metal charge into the periclase (MgO)-lined converter with the vessel cinder; the overlap or readjustment step consists of waiting until the silicon and manganese content of the fresh, hot metal have caused the reversion of the phosphorus and iron from the overblown vessel cinder.

The readjusted phosphorus-free overlap slag or "synthore" is finally poured or raked from the converter and the first step is repeated, and so on. In this way, it is possible to remove from the bath as much as ninety five percent of the manganese which would be true in the case of blowing a metal containing twenty percent of manganese down to 0.5 percent of manganese.

The above-described process of selective oxidation, as presently developed, has a number of inherent defects which preclude its use on a commercial scale, these defects are as follows:

All of the subject ores and materials must be smelted, and whatever manganese is recoverable in this step must first be reduced to the metallic state. Most of whatever manganese is recovered in the initial smelting of the subject ore is then oxidized into a slag of high iron and phosphorus content; then both the phosphorus and iron must be selectively reduced from the converter slag; and finally this relatively phosphorus-free, selectively reduced converter slag must subsequently be smelted into a ferro-alloy. Should each of these four metallurgical functions be performed with a recovery of seventy percent of the subject manganese, which probably is possible, the actual recovery of the manganese from the original ore would be $.7 \times .7 \times .7 \times .7 \times 100$, or only about twenty-four percent. Even were one of these steps perfected to operate consistently at ninety percent of total recovery, two-thirds of the original manganese would still be irrecoverably lost.

In the violent process of blowing air through the molten metal in the converter, much metal fog (exceedingly fine particles of metallic iron) is emulsified with the vessel

cinder. Unless the cinder is very fluid, and sufficient time is allowed for the settling-out of the metal fog, the vessel cinder will not be low enough in phosphorus and iron to produce a ferroalloy which will meet A.S.T.M. specifications.

Since all of the subject ores must be smelted and the reducible oxides first converted into the metallic state, an inordinate amount of metallurgical fuel is required which would, in any cases, render the selective oxidation process too costly to become an economic method of recovering manganese from steel plant wastes and/or contaminated ores.

In the process of selective oxidation as presently developed, only those plant wastes and ores which contain upwards of eight or ten percent of manganese (flush slag) can be considered as potential sources of this element. Thus, at the present stage of development, fully half of the manganese wasted in open hearth slags is beyond recovery by any prior known process, since the manganese content of the greater portion of steel plant wastes is below five percent of manganese.

The most serious objection to the batch process of selective reduction of phosphorus and iron from the vessel cinder in the overlap step of the process described above is that silicon cannot distinguish between iron and phosphorus and reduces either to the bath indiscriminately, depending upon which happens to be available for reaction, and is wasteful of the thermodynamic potential of silicon (9600 B.t.u. per pound between Si and SiO_2) and cannot make full use of the manganese potential (1869 B.t.u. per pound between Mn and MnO) and the reduction of FeO to Fe (1230 B.t.u. per pound of Fe). P_2O_5 requires the potential of silicon for reversion and this is why some silicon is used in the reagent metal, but only enough silicon to cause the exchange of phosphorus is necessary.

In respect to recovery of manganese, my invention eliminates all of the inherent defects of the prior art selective oxidation processes which are enumerated above.

In my continuous hearth, steel refining and manganese ore decontamination and beneficiating method, I enumerate the following improvements:

The manganese ore is not exposed to the possibility of metallurgical loss during its decontamination and coincidental enrichment, and the recovery in this step is one hundred percent of the original manganese. The overall recovery of the manganese from the subject ore in the form of ferromanganese is a function of the final smelting step alone.

The manganese ore is not initially smelted into metal; and, aside from the heat used to melt the ore (anthracite coal will serve in the melting cupola), no metallurgical fuel is required in the decontaminating and enriching step. Thus, a very great saving in metallurgical coke is effected.

The reagent metal need not be rich in manganese. For instance, in my process as much as ninety percent of the manganese ordinarily contained in pig iron (Eastern practice) can be recovered in usable form, incidental to the continuous refining of pig iron into steel.

My invention provides a suitable method and apparatus for the decontamination and enrichment of manganese ores and material which may not otherwise be fully acceptable for the production of ferroalloys; and to accomplish this decontamination and enrichment incidental to the refining of steel from molten ferrous alloys such as pig iron or any kind or type of spiegeleisen.

My invention generally contemplates a basic lined reverberatory furnace which is long in proportion to its breadth. The furnace is adapted to contain a metal bath which is shallow in respect to its width. A reagent underflowing metal and floating manganese ore are continuously poured into opposite ends of the furnace to flow in opposite directions; and the rate of flow of metal is sufficient to exceed the rate of diffusion and/or longi-

tudinal mixing of the molten metal. The rate of flow of slag over the metal is rapid enough that chemical equilibrium of the reactions between the constituents in the slag and metal cannot be approached, i.e., the relative counter flow of slag and metal at optimum rate would be such that the maximum imbalance is maintained between the reacting metals and metalloids and their oxides, so that the desirable reduction of iron, phosphorus and other contaminants may proceed at the highest rate. Coincidentally, manganese will be oxidized from the reagent metallic bath to the molten subject ore floating above the metal interface; and this maximum imbalance is maintained until the phosphorus, iron and other contaminants have been reduced from the slag to the metallic underflow and coincidentally until all oxidizable manganese has risen from the metal to replace the iron oxide in the floating molten ore.

In my continuous hearth apparatus, the area of interface of slag and metal through which the principal reactions occur is at least twice as great in proportion to the volume of metal as compared to the currently standard open hearth furnace. Relative rates of flow at the interface of at least two feet a minute will sustain the maximum chemical potentials, and favor the complete and rapid impoverishment of silicon and manganese from the metal and the coincidental decontamination of the molten floating ore from the iron, phosphorus and other deleterious elements.

Due to the counter flow of slag and metal, the manganese metal will react principally with the iron oxides, and the silicon metal will react mainly with the phosphorus oxides. As the metal enters the continuous hearth, it flows under molten ore which already has most of its FeO replaced by MnO due to the counter flow of slag and metal. Since the fresh metal is rich in silicon, it reacts with the phosphorus oxides, almost completely eliminating the latter from the ore. As the reagent metal continues its flow through the hearth, its silicon is soon expended and the manganese reacts with and replaces the FeO in the slag. Thus, the reduction of phosphorus is accomplished by the oxidation of silicon; and manganese is oxidized largely by the iron oxides, as the result of the maintenance of adequate counter flow rates of molten ore and reagent metal.

In my preferred method, both the subject ore and reagent metal are introduced into the continuous hearth at temperatures well above the respective melting points and maintained at 2900° F., plus or minus about 150° F. depending upon the desired analysis of the products. Since the thermal sum of the chemical reactions taking place between slag and metal is exothermic, the heat to be supplied to the continuous hearth is somewhat less than the total heat lost to the surroundings and to the atmosphere.

The objects of this invention are as follows:

To provide a steel refining method and apparatus which will automatically separate the traditionally wasted manganese from phosphorus and increase the conservation and utilization of both. At least a half-million tons of metallic manganese and more than three-quarters of a million tons of phosphate fertilizer containing twenty percent P_2O_5 are currently wasted each year in open hearth slag.

To provide an apparatus capable of decontaminating and beneficiating large tonnages of manganese ore and which may be readily controlled and economically maintained.

To provide a method and apparatus in which manganese ore is decontaminated of iron, phosphorus and other elements and coincidentally is enriched in the amount by which metallic oxides, such as FeO, are replaced by MnO derived from a reagent metal bath.

To provide a method and apparatus whereby contaminated manganese ore can be made relatively free from iron, phosphorus and other readily reducible contami-

nants, and in the same continuous process, produce iron for ingot steel or for high grade electric furnace melting stock which can be made substantially free from silicon, manganese, phosphorus, sulphur and carbon. In the same continuous process, phosphorus can be recovered in a valuable, salable form.

To provide a method and apparatus in which manganese ore may be enriched at the expense of the manganese content of any hot metal which contains more than one-half of one percent of manganese as metal.

To provide an apparatus which will afford the means whereby a continuous stream of molten ore may be caused to flow over the surface of a molten countercurrent stream of metal in such a manner that the chemical potential between the reactants in the slag and metal can be kept in the maximum possible state of imbalance in order to favor immediate and complete reaction.

To provide a method and apparatus in which the subject ore is decontaminated and coincidentally enriched, yet the overall recovery of manganese from the subject ore in the form of ferroalloys is a function of the final smelting step alone.

To provide a method and apparatus for the recovery of manganese from contaminated and/or low grade ores incidental to the refining of steel from ferrous alloys in which the fuel and/or energy requirement is uncommonly small per unit of manganese recovered and per ton of steel refined.

To provide a method and apparatus in which at least two slags are separately and continuously produced; and in which one of these slags will contain practically all recoverable manganese, and the other will contain practically all the phosphorus from the metallic underflow.

To provide a method of selectively utilizing the chemical potential of silicon to de-oxidize phosphorus from molten manganese ore and in the same molten bath to cause manganese to de-oxidize iron oxide in the molten manganese ore and to replace iron oxide with manganese oxide mol for mol in the slag (molten manganese ore) to the extent to which manganese is oxidizable from the metal; and by the flexibility of the counter current process cause metal to flow under the slag and in relation to this slag in the amount necessary for replacing all free iron oxide (which is not combined as a silicate) with manganese oxide, regardless of the weight percent of manganese originally contained in the reagent metal.

Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings, which disclose by way of example, the principle of the invention and the best mode which has been contemplated of applying that principle.

In the drawings:

FIG. 1 is a sectional elevation view of a preferred form of a continuous hearth furnace in operation, which furnace is usable in practicing the process of this invention;

FIG. 2 is a sectional view taken along line 2—2 of FIG. 1;

FIG. 3 is a sectional view taken along line 3—3 of FIG. 1;

FIG. 4 is a schematic illustration of the use of a pair of continuous hearth furnaces for first enriching and decontaminating manganese ore and subsequently producing refined steel from the reagent metal;

FIG. 5 is a graphical illustration of the chemical balance of the metals and metalloids in the molten slag which is being enriched and decontaminated and in the molten reagent metals as a counterflow in the continuous hearth;

FIG. 6 is a graphical representation of the chemical constituents of a molten metal being de-phosphorized, desulphurized and de-carbonized along the length of a continuous hearth in the refining of steel.

Referring to the drawings, FIG. 1, a reverberatory-type continuous hearth furnace is indicated generally at 10. Molten slag and metal may be continuously poured

or fed at a controlled measured rate into this furnace at opposite ends thereof and may be continuously and separately withdrawn therefrom after flowing through the furnace countercurrently. The feeding rate of the ore or slag and the molten reagent metal can be regulated, and the velocities of the countercurrent flow can be varied. The depth of the metal bath can be adjusted and maintained at any given level, as can the depth and level of the molten ore or covering slag.

The furnace 10 includes a refractory hearth 12 covered by a sectionalized removable refractory top 14. End walls or arches 16 and 18 are provided at each end of the top 14. The portion of the hearth 12 extending beyond the end walls 16 and 18 constitutes two forehearth 17 and 19.

The level of the reagent metal in the hearth is governed by a metal dam 22 over which the metal may flow into a suitable ladle 28. The level of the molten ore or slag is determined by the height of a refractory metal dam 24 and thus may be suitably regulated. Molten ore or slag to be decontaminated and enriched is poured into the hearth from a suitable ladle 30 and is prevented from flowing over the dam 22 by a refractory skimmer 26 under which the reagent metal can freely flow. Lips 25 and 27 assist in tunneling the molten metal and ore into slag pot 36 and ladle 28, respectively.

Heat is applied to the furnace by direct arcs struck to the melt from one or more sets of electrodes 20 which are inserted through apertures in the refractory roof sections 14. Alternatively, heat may be supplied to the furnace in a manner similar to that used in heating open hearth furnaces if regenerative checker brick heat exchangers are supplied. The heat is supplied only to replace the heat lost to the surroundings and the way of applying this heat is not critical, although electric heating is the preferred embodiment because regenerative heating may cause the introduction of undesired sulphur and pose a fume problem.

The hearth is made readily accessible for inspection and repair by lifting off the roof sections 14 and by drawing the molten contents through suitable tap holes 32 which are provided for this purpose. Molten reagent metal may be poured into the continuous hearth at a controlled rate from a suitable ladle 34, and the decontaminated and enriched slag may be removed after it flows over dam 24 in slag pots 36.

The operation of the apparatus described in FIGS. 1-3 for the decontamination and coincidental enrichment of manganese ore will now be described. Molten metal such as spiegeleisen or pig iron is poured continuously at a measured rate from ladle 34 into the forehearth 19; simultaneously and continuously, molten manganese ore is poured from ladle 30 into forehearth 17 between the skimmer 26 and the end wall 18 of the reverberatory hearth furnace 10.

The molten manganese ore flows from left to right as viewed in FIG. 1, and the molten reagent metal flows from right to left as viewed in FIG. 1. The ore will flow on top of the reagent metal, and there is a wide area of interface therebetween. The molten ore or slag thus flows countercurrently over the reagent metal. As shown in FIG. 5, the incoming reagent metal contains enough silicon to exchange with the phosphate in the outflowing slag and then remove the contaminating phosphorus from this slag as the reagent metal flows along farther, its manganese will exchange with the iron oxide in the slag to accomplish the preferential molal exchange of manganese and iron. After being decontaminated of phosphorus and enriched with manganese, the slag flows over dam 24 and lip 25 into slag pot 36. The metal stream flows continuously countercurrently under the molten ore and passes under the skimmer 26 over the dam 22 and the lip 27 into a metal ladle 28.

The pouring rate of the metal from ladle 34 is regulated relative to the pouring rate of molten ore from ladle 30 such that the manganese content of the molten metal

reaching ladle 28 has been reduced to the desired point and the molten ore reaching slag pot 36 has been enriched to the desired grade, and the phosphorus and iron contents thereof have been reduced to required limits.

The decontaminated and enriched molten ore is transferred from the slag pot 36 to a cooling pit. It is then suitably broken and may be utilized as the ore for the production of phosphorus-free ferroalloys.

The reagent metal which flows over dam 22 into ladle 28 is high in phosphorus and carbon. This molten metal is subsequently treated to dephosphorize it, and to decarbonize and desulphurize it if necessary in a second continuous hearth furnace similar to the furnace illustrated in FIGS. 1-3. However, other known steel refining processes may be used where close control for dephosphorizing, decarbonizing and desulphurizing is not essential. The entire operation of decontaminating and enriching the molten manganese ore in a primary continuous hearth furnace and subsequently dephosphorizing and decarbonizing and desulphurizing the molten metal in a second continuous hearth furnace is shown schematically in FIG. 4 and graphically in FIGS. 5 and 6.

As shown in FIG. 4, the molten reagent metal M-1 flows countercurrently under the molten slag or manganese ore S-1 in the continuous hearth furnace 10 to react therewith and produce decontaminated slag S-2 enriched in manganese and molten metal M-2 which remains high in phosphorus and carbon. The molten metal is then reacted with a basic slag S-3 and another continuous hearth reverberatory furnace 10' identical to the furnace 10. A typical reaction is shown in FIG. 5, wherein the abscissa is equal to the length of the open hearth and the ordinate represents the percentage of materials. At the left-hand side of the hearth, the fresh incoming slag reacts with the outgoing metal, and at the right-hand end of the furnace, the outgoing slag reacts with the incoming metal. The incoming reagent metal withdraws the phosphorus from the slag by the reaction of silicon with P_2O_5 and thus almost immediately withdraws the phosphorus from the slag to an amount not greater than 0.1% as shown in FIG. 5. Higher temperatures favor the formation of Fe_3P from phosphates. The dephosphorized slag then flows out. Further along in the flow of the reagent metal, the manganese in the reagent metal reacts with the iron oxide in the slag and exchanges therewith, thus withdrawing the iron from the slag to the metal and withdrawing the manganese from the reagent metal to the slag. Hence, the slag is enriched in manganese and has a large portion of the iron removed therefrom. The incoming molten manganese ore, therefore, sees the spent reagent metal which has much of its manganese already withdrawn but has taken some of the iron and also most all of the phosphorus from the molten slag. The silicon, however, in the metal at the outlet side is almost completely eliminated because the amount of silicon originally in the reagent metal is only slightly greater than the amount necessary to withdraw all the phosphorus from the slag.

The phosphorus collected in the reagent metal M-2 is not detrimental to my steelmaking process as it has sufficient potential for its own removal when reacting with a basic slag such as slag S-3.

In the operation of dephosphorizing, decarbonizing and desulphurizing of the metal M-2 from which the silicon and desired amount of manganese have been removed in the continuous hearth furnace 10, metal M-2 is poured into one end of the furnace 10' on the forehearth, and simultaneously, calcined limestone is fed into the other end of the furnace on the forehearth between the refractory skimmer and the end of the furnace. Because burnt lime without iron oxide can be added to the metal bath following the elimination of the major portion of the phosphorus, sulphur removal is favored at the right-hand end of the continuous hearth furnace 10'. About twenty percent further to the left along

the length of furnace 10', iron oxide and some silica are added to the burnt lime originally added for desulphurizing; this basic flux is at least two CaO to one SiO_2 , and it flows countercurrently over the metal M-2 to effect phosphorus removal from the metal, this is shown graphically in FIG. 6. The calcined limestone may be raked off through the side of the furnace as the dephosphorizing basic slag is added.

The rate of flow of the countercurrent streams in furnace 10' is regulated and is principally a function of the rate of removal of sulphur and phosphorus from the underflowing metal into the overflowing slag. The basic slag which flows out the end of furnace 10' as indicated at S-4 contains calcium sulphide and soil available calcium phosphate. The dephosphorized, desulphurized metal which flows out the other end of the continuous hearth 10' indicated at M-3 may be cast into molds for steel melting stock or ingots.

If it is necessary to reduce the carbon in the metal M-3 to very low limits, oxygen may be blown into the metal stream inside the furnace near the point where the second fluxing addition is made. This also will promote the more complete elimination of phosphorus. The desulphurizing step in furnace 10' may not be necessary if no sulphur has entered the process. In this case molten basic slag is poured at a controlled rate on the forehearth of furnace 10' to flow countercurrently to the incoming metal for dephosphorizing purposes.

The continuous hearth furnaces 10 and 10' need not be on different levels as shown schematically in FIG. 4, and the ladle for the metal 28 in FIG. 1 may not be used when the continuous hearth furnaces 10 and 10' are set up in series. If the furnaces are on the same level, the metal dam 22 and lip 27 are unnecessary.

It has been demonstrated in open hearth practice that the output of a furnace is directly proportional to the area of interface per unit weight of metal in the furnace. Therefore, by keeping a large interface area in proportion to the metal in the furnace at any one time my process will have a relatively large capacity with a relatively small furnace and hence reduce the capital cost of steelmaking.

The rate of flow of the metal and slag in each continuous hearth furnace exceeds the rate of diffusion or longitudinal mixing, and equilibrium cannot be approached between the elements in the slag and metal. Therefore, the elements are kept at their maximum chemical imbalance by the relative counterflow. Thus, sufficient chemical potential exists without additional energy in the order of that required for melting to promote all reactions between the slag and the metal. Hence, the direct arc struck to the bath furnishes heat to supply heat lost to the surroundings and maintain the optimum reaction temperatures. In other words, mine is a "downhill" process not requiring a large amount of heat energy.

The superfluent slag may or may not be caused to flow continuously relative to the furnace, but it does always flow continuously relative to the affluent metal. No additions may be made of subject ore for a time while metal may continue to flow under the slag to effect complete removal of the phosphorus from the superfluent slag and complete replacement of free iron oxide by manganese oxide. Conversely, the slag may flow over the metal for a time with no metal additions to the continuous hearth and a temporary static reagent metal bath.

Nevertheless, there is continuous longitudinal displacement between the superfluent molten subject ore (slag) and the reagent metal (pig iron, spiegeleisen, etc.), although one or the other may remain stationary for a time in respect to the furnace.

It is to be noted that small chemical potentials keep the process moving by virtue of the counterflow which maintains maximum chemical imbalance and allows the spent reagent and enriched reactant to be continuously removed.

The invention is illustrated further, but is not limited by the following practical example.

Example

A manganese ore which may be relatively low grade is melted and is poured from a ladle into one end of the continuous hearth furnace. This ore may have the following composition: MnO—17.0%; FeO—29.6%; P (as P_2O_5)—1.4%; SiO_2 —30.0%; Al_2O_3 —2%; CaO—15%; MgO—5.0%. Thus, the ore is approximately 13% Mn and 23% Fe. The molten ore is poured from the ladle at the rate of approximately sixty tons per hour.

A reagent metal which may be substandard pig iron having approximately the following analysis: Mn—8%; Fe—83.5%; P—2%; C—4%; Si—2.5%; is produced from three tons basic open hearth slag and one ton of scrap from a blast furnace and is taken molten from the blast furnace to a hot mixer and poured from the ladle into the continuous hearth furnace at the rate of approximately one hundred twenty tons per hour. In the continuous hearth furnace, the subject ore flows countercurrently to the reagent metal and reacts therewith at the maximum chemical imbalance.

As can be seen from the above and especially with reference to FIG. 5 of the drawings, the silicon in amount in the entering reagent metal is sufficient to pull the phosphorus down from the slag but is not substantially in excess of this amount as such would be detrimental to the slag. Further, the silicon phosphorus exchange has the effect of reducing the phosphorus in the slag to 0.1% or less.

In the example, the enriched and decontaminated ore of ferro manganese contains approximately 33%—MnO; 6.4%—FeO; 43%— SiO_2 ; 0.1%—P; Al_2O_3 ; 12%—CaO; 3.5% MgO. Thus, the decontaminated enriched ore contains about 26% manganese and 5% iron. This ore may be stockpiled at the rate of sixty-two tons per hour if the feeding rate is as set out above. The heat of the furnace may be approximately 2950° F., and may be maintained by supplying only the heat lost to the surroundings e.g. 70,000 B.t.u. per hour per foot of hearth length. The reagent metal M-2 which is now relatively high in phosphorus and carbon and may incidentally have picked up some sulphur if a sulphur containing fuel is utilized, or is contained in recirculated scrap added to continuous hearth 10' with molten metal M-2. This metal is now fed to a second continuous hearth 10' for dephosphorizing, desulphurizing and decarbonizing. In this second hearth 10', the reagent metal, is fed at one end, and calcined limestone is fed at the other end. Further along in the second continuous hearth, iron oxide and some silica are added to the calcined limestone burnt to produce a dephosphorizing slag or the calcined limestone may be raked off and a molten basic slag is added to effect removal of the phosphorus from the metal. The products of the second continuous hearth are a slag which contains soil available tri-calcium phosphate and may be commercially usable, and a high-grade steel which may be poured into molds and utilized as special electric furnace melting stock or may be put into a teeming ladle, and ferroalloys may be added thereto to produce ingot steel.

The heat required per ton of metal and slag passing through the continuous hearth would vary inversely as the rate of flow. For example, in the continuous hearth furnace having a slag-metal interface width of eight feet, the heat losses to the surroundings are about 70,000 B.t.u.'s per hour per foot of hearth length and an internal temperature of 2900° F. In a sixty foot continuous hearth, the flow rate of metal could be 120 tons an hour and the counterflow rate of molten ore could be 60 tons an hour. If the ore is alone chargeable for the heat supplied, then per ton of ore decontaminated, the thermal input is 70,000 B.t.u.'s per ton or about 21 kilowatts of electric power. However, since the metal is also later re-

fined to steel, the ore should be charged only one-third of this.

However, both slag and metal, or either, may be introduced into the continuous hearth, dry but unmolten. A corresponding additional amount of thermal energy must be supplied to melt the cold material.

While the process has been described in connection with the beneficiation and decontamination of manganese ores and the refining of steel, it will be apparent that the process also has utility in the molal exchange reactions of other metals and slags which reaction occur on a preferential basis. For example, this preferential mold pyrometallurgical principle may also be advantageously applicable to metals and ores of nickel, cobalt, chromium, silicon and iron complex.

While there have been shown and described and pointed out fundamental novel features of the invention as applied to the preferred embodiment, it will be understood that various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art without departing from the spirit of the invention. It is the intention, therefore, to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. A pyrometallurgical process for decontaminating and coincidentally enriching low-grade manganese ore by preferential molal exchange, said method comprising: continuously introducing molten phosphorus and iron containing manganese ore and molten reagent metal containing iron, manganese and amount of silicon slightly in excess of the amount necessary to exchange with all of the phosphorus in the ore, into opposite ends of a continuous hearth metallurgical furnace to produce counterflow thereof across a wide interface area, maintaining the desired temperature for maximum reaction between 2750° F. and 3050° F. whereby the small amount of silicon in the reagent metal will first react with the outflowing superfluent molten ore to exchange with the phosphorus therein, reducing the phosphorus content of the ore to no greater than 0.1%, continuing the counterflow at a rate that exceeds the diffusion and mixing of the counterflowing layers of ore and reagent metal and at such a rate that chemical equilibrium is not reached, reacting the manganese in the incoming reagent metal with the iron in the ore to thereby enrich the ore with manganese and decontaminate the ore of phosphorus, and removing the spent reagent metal and enriched phosphorus free ore from opposite ends of said furnace.

2. A method as defined in claim 1 further comprising reacting the resultant molten metal which is high in phosphorus and carbon with a basic slag by a continuous counterflow process to thereby reduce the phosphorus and carbon content of the molten metal for producing a steel in an additional continuous hearth furnace.

3. A method as defined in claim 2 further comprising adding molten recirculating scrap to the molten metal, and adding calcined limestone to the counter-flowing slag to desulphurize the molten metal.

4. A continuous process for the production of phosphorus free high manganese slag from a low grade molten manganese ore by preferential molal exchange, the process comprising: introducing a molten manganese ore containing iron and phosphorus continuously into one end of a long, shallow reverberatory hearth furnace and introducing a molten reagent metal having iron, manganese, and a small amount of silicon slightly in excess of the amount required to exchange with all the phosphorus in the ore into the other end of said furnace whereby the molten ore will flow above and countercurrent to the molten metal, establishing a continuous large-area interface for molal exchange between the molten ore and metal and maintaining the ore and metal at a temperature between 2750° F. and 3050° F. whereby the silicon in the molten reagent metal will first exchange with phos-

phorus from the molten ore and decontaminate the outflowing ore of phosphorus to an amount not greater than 0.1% and subsequently the manganese in the molten reagent metal will exchange with the iron in the molten ore to thereby enrich the molten ore with manganese, and continuously removing the enriched and phosphorus free molten manganese ore.

5. A process of obtaining low-phosphorus enriched manganese slag from manganese ore by preferential molal exchange that comprises; melting said low grade manganese ore having iron, manganese and phosphorus therein and melting a reagent metal having iron, manganese, and some silicon therein, the amount of silicon being only slightly in excess of the amount required to exchange with all of the phosphorus in the ore, continuously introducing said molten ore in the form of a slag and molten metal into opposite ends of a reverberatory continuous hearth furnace to produce a counterflow therebetween across an interface of large area, introducing heat into said furnace to contribute the heat lost to the surroundings and maintaining the temperature between 2750° F. and 3050° F., preferentially exchanging the phosphorus in the slag with silicon in the reagent metal as the incoming reagent metal contacts the outgoing slag during the counterflow and the iron in the slag with manganese in the metal as the incoming ore contacts the outgoing metal, thus reducing the phosphorus content of the ore to an amount not greater than 0.1%, and continuously removing the decontaminated and enriched manganese slag and the molten metal, now high in phosphorus exchanged from the slag.

6. A process of refining steel from a metal containing iron, manganese, carbon, and a small amount of silicon, said process comprising; melting said metal, forming a molten slag, said slag containing iron and phosphorus, the amount of silicon in the metal being only slightly in excess of the amount required to exchange with all of the phosphorus in the slag, counterflowing said slag and said molten metal from opposite ends of a continuous hearth furnace, maintaining the temperature of the slag and metal at a level between 2750° F. and 3050° F. to promote preferential molal exchange of the silicon in the molten metal with the phosphorus in the slag to reduce the phosphorus content of the slag to an amount not greater than 0.1% and the manganese in the molten metal with the iron in the slag, thereby dephosphorizing the slag and coincidentally enriching the slag with manganese and withdrawing additional iron from the slag into the molten metal, removing said molten metal and said slag and introducing said molten metal into another continuous hearth surface, while also introducing a basic slag into said second continuous hearth furnace whereby said basic slag will react with the molten metal during counterflow relative thereto, to remove the phosphorus therein, introducing an oxygen-containing gas into said second continuous hearth furnace to remove some of the carbon from the molten metal, and removing the molten metal from said second continuous hearth furnace, said

molten metal now being free of phosphorus, carbon, silicon, and manganese to the required limits.

7. A process for continuous hearth refining of steel and beneficiation of ores of ferro-alloys, said process comprising; introducing into opposite ends of a continuous hearth furnace a molten reagent metal and a molten slag, said molten reagent metal containing iron, manganese, silicon, carbon and phosphorus, said molten slag containing manganese, iron and phosphorus, the amount of silicon in the reagent metal being only slightly in excess of the amount required to exchange with all of the phosphorus in the molten slag, establishing counterflow in said continuous hearth furnace between said molten slag and molten reagent metal across a wide area of interface which is large in proportion to the weight of metal and slag in the furnace at any one time, and maintaining the temperature of the molten slag and molten reagent metal between 2750° F. and 3050° F. whereby the silicon in the reagent metal will react with the phosphorus in the molten slag as soon as the reagent metal is introduced, reducing the amount of phosphorus in the slag to not greater than 0.1% and the manganese in the reagent metal will exchange with the iron in the molten slag after the exchange of phosphorus and silicon and as soon as the molten slag is introduced, continuously removing the relatively phosphorus free reacted slag which is coincidentally enriched with manganese, and continuously removing the reacted reagent metal which now contains additional iron and phosphorus from exchange with the molten slag but is relatively free of silicon and manganese, introducing said reacted metal having silicon and manganese content reduced to desired limits into a second continuous hearth furnace at one end thereof, and introducing a basic slag to the other end of said continuous hearth furnace and establishing counterflow therebetween, whereby the basic slag will react with the molten metal during the counterflow to remove the phosphorus therefrom, introducing oxygen containing gas into said second continuous counterflow to deoxidize and aid in dephosphorizing the reagent metal, and removing the metal having the phosphorus, manganese, carbon and silicon contents reduced to desired limits from the second continuous hearth while also removing the slag containing the phosphorus from the second continuous hearth.

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