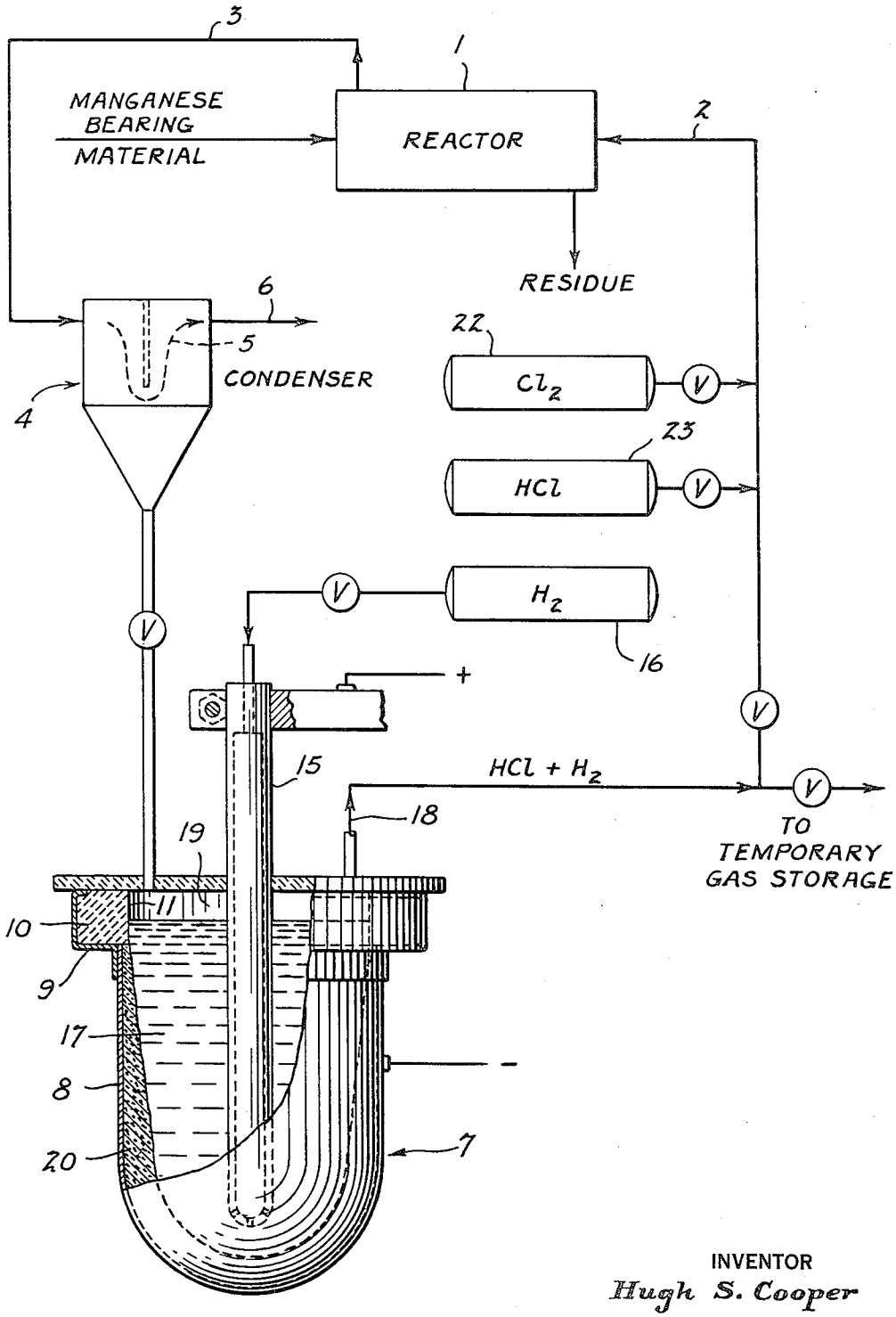
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ELECTROLYTIC PRODUCTION OF MANGANESE AND FERROMANGANESE

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ELECTROLYTIC PRODUCTION OF MANGANESE AND FERROMANGANESE

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This invention relates to the recovery of substantially pure, carbon-free manganese and iron powders and ferromanganese powder from various materials containing both iron and manganese associated with one or more undesirable materials.

At the present time, high grade manganese ores are commercially reduced by controlled smelting operations to produce ferromanganese having various carbon contents ranging from about .07% to 10% or so. The smelting operation is reasonably efficient and economical for the production of relatively high carbon ferromanganese, but the cost of producing low carbon ferromanganese, which requires the use of an electric furnace, has been undesirably high. The present commercial high carbon ferromanganese can be used for general steel making purposes, but a low carbon ferromanganese alloy is required in the production of steels having high manganese content because of the strict limitations on the permissible carbon content of such steels.

Manganese metal has also been produced commercially to some extent from both high and low grade ores by electrodeposition from aqueous solutions. The cost of this process, however, is so great as to render the product too expensive for anything but special uses in relatively small quantities where the cost of the manganese is not an important factor. The production of manganese by electro-deposition from aqueous solutions is apparently incapable of competing with current smelting operations for producing manganese for general use in the alloy steel industry.

A number of materials containing substantial quantities of manganese and iron are available in abundant quantities in the United States. Examples of these are the low grade manganese ores and the slags from steel making operations. Standard, high carbon ferromanganese, presently being produced by efficient smelting operations, is also available in more limited quantity as a source of manganese. However, in spite of intensive work on the problem, no commercially successful processes have yet been devised for recovering manganese or ferromanganese of either low or high carbon content from low grade domestic ores or steel slags.

Unfortunately, the United States has very little manganese ore of high grade and must import from foreign sources most of the manganese ores required to satisfy its present needs. Accordingly, the need for an economical process for recovering manganese and ferromanganese from the low grade ores and steel slags is manifest.

Thus, there has long been a need for an economical and efficient process for producing manganese or ferromanganese in a substantially pure form, and there is an even more urgent need for a process capable of economically recovering manganese and low carbon ferromanganese from low grade ores and steel slags.

Depending upon the character of the starting material and the use for the recovered manganese, it may or may not be desirable to retain all of the iron content of the

starting material with the manganese. Since there is a rapidly growing demand for pure iron powder, which commands a substantial price on the market, any iron recoverable in the form of a pure powder is of great commercial value and contributes substantially to the economy of the overall process for producing the manganese product.

The principal object of the present invention is to provide a process for recovering pure manganese and iron or pure ferromanganese, or all three, from impure materials containing manganese and iron in elemental or oxide forms.

A more specific object of the invention is to provide a process for producing pure ferromanganese containing manganese and iron in any desired ratio.

Still another object of the invention is to provide a process for treating materials containing impure manganese and iron in elemental or oxide forms, so as to recover substantially all of the manganese and iron available in the starting materials, either separately as pure elemental manganese and iron powders, or together as pure powdered ferromanganese, or any combination thereof.

Still another object of the invention is to provide a process for treating ores or slags containing manganese and iron in the form of oxides to recover the manganese and iron in a substantially pure powdered form, either separately or as an alloy, or both.

Still another object of the invention is to provide a process for treating high carbon ferromanganese to recover the manganese and iron in a substantially pure powdered form, either separately, or as an alloy, or both.

A further object of the invention is to accomplish the foregoing objectives in a manner that is sufficiently simple and economical to permit the products to be sold at prices consistent with their value to industry.

While this invention finds its greatest commercial utility in the recovery of manganese and iron from low grade ores and slags, the process is sufficiently economical and flexible so that it may be competitively employed, with certain variations, to produce substantially carbon-free manganese and iron powders or powdered ferromanganese alloys from high grade ores and from commercial, high carbon ferromanganese produced by other processes.

The process of the present invention, as applied to the treatment of oxide ores and slags, involves contacting the starting material with a suitable chloridizing reagent at an elevated temperature under completely anhydrous conditions and in the absence of any reducing agent. The suitable chloridizing reagents are anhydrous chlorine, hydrogen chloride, and mixtures thereof.

By controlling the temperature of the chloridizing treatment and by selecting the proper chloridizing reagent, the iron and manganese may be chloridized and sublimed individually or in any desired proportions as substantially pure metal chlorides. If the iron and manganese chlorides are sublimed together by the selection of an appropriate chloridizing reagent and an appropriate chloridizing temperature, the mixture of sublimed chlorides may be sharply separated by fractional condensation, or either one of them may be partially separated and condensed and the balance of them condensed together as mixed chlorides.

The chloride products are substantially completely anhydrous and may be disassociated by fused bath electrolysis in a special electrolytic cell, either separately or admixed together in any desired proportions, to produce the metal or metals in substantially pure powdered form. When the mixed chlorides are electrolyzed, the metallic deposit recovered from the electrolytic cell is a pure powdered alloy of the two metals in substantially the

same proportions present in the electrolytic bath. Hydrogen gas is introduced into the fused bath during electrolysis to take up the liberated chlorine and, as a result, anhydrous HCl is recoverable from the electrolytic cell and may be recycled for use alone or in admixture with chlorine for chloridizing additional ore or slag.

The process of the invention as applied to the treatment of high carbon ferromanganese is basically the same, except that some carbon (normally a reducing agent) is necessarily present by reason of the carbon content of the starting material. When treating ores or slags containing other oxides than those of manganese and iron, the absence of a reducing agent is important in order to avoid chloridizing the other oxides with serious consequences discussed hereinafter. However, when treating high carbon ferromanganese in which carbon is substantially the only contaminant, this precaution is unnecessary, since the chloridizing reaction is carried out in the substantial absence of oxygen and the carbon remains behind in the chloridizing chamber.

Whether the material to be chloridized is an oxide ore or slag or is a high carbon ferromanganese, pure, anhydrous HCl is generally the preferred chloridizing reagent, though chlorine gas may be used for this purpose in a number of instances. Anhydrous HCl reacts with iron and with iron oxide to produce $FeCl_2$, whereas chlorine reacts under similar conditions to produce $FeCl_3$. Both chloridizing reagents react with manganese and with manganese oxide to produce $MnCl_2$. Since less power is required to reduce $FeCl_2$ than $FeCl_3$ in an electrolytic cell, and since anhydrous HCl is recovered from the electrolytic cell in a form suitable for reuse to chloridize additional manganese and iron, anhydrous HCl is the most economical and practical chloridizing reagent for most operations.

However, when using HCl as the chloridizing reagent, $MnCl_2$ and $FeCl_2$ are formed and sublimed at temperatures sufficiently close to make fractional sublimation and fractional condensation difficult. On the other hand, when using chlorine as the chloridizing reagent, $FeCl_3$ may be formed and sublimed efficiently at temperatures well below the temperature at which $MnCl_2$ will sublime. To illustrate, $FeCl_3$ begins to sublime at about 315° C., $FeCl_2$ at about 680° C., and $MnCl_2$ at about 700° C. (Most published data give the boiling point of $MnCl_2$ as about 1190° C., but I have found that it actually begins to sublime at a temperature as low as 700° C.)

Thus, by first employing chlorine as the chloridizing reagent at a relatively low temperature, any desired proportion of the iron in the starting material may be sublimed and condensed as $FeCl_3$, whereupon the remaining iron, if any, and the manganese may be chloridized and sublimed together at a higher temperature by the use of either chlorine, HCl, or a mixture thereof. Because HCl is preferred for most other purposes, as explained above, the chloridizing agent should generally be at least partially changed from chlorine to HCl after the desired amount of pure $FeCl_3$ has been preliminarily formed, sublimed from the reactor, and separately condensed. As will be apparent, either chlorine, HCl, or mixtures thereof may be employed at temperatures sufficient to form and sublime $MnCl_2$, together with $FeCl_3$ or $FeCl_2$ or both, depending upon whether or not any iron or iron oxide is still present in the material being treated and depending upon the particular chloridizing reagent employed. As further explained hereinafter, such temperature should be above about 800° C. and preferably about 1100° C.

The foregoing and other objects, advantages, and characteristic features of the invention will be better understood from the following more detailed description of illustrative applications of the invention to specific recovery problems, and from the accompanying drawing in which a flow diagram for the system and certain preferred details of an electrolytic cell for use therein are shown.

Treatment of ores

Both high and low grade manganese ores of the oxide type contain manganese and iron oxides together with impurities, such as silicon dioxide, aluminum oxide, and phosphorus. The ratio of manganese to iron in these ores generally ranges from about 3:1 to about 6:1, so that recovery of both the manganese and iron contents thereof in the form of ferromanganese will yield an alloy having a commercially useful manganese content without the necessity for separating any substantial amount of the iron during the process.

To produce a carbon-free ferromanganese from such ores in accordance with the present invention, the ores are reduced to a finely granular condition and are heated in a suitable reactor, in the absence of any reducing agents and with the substantial exclusion of atmospheric oxygen and moisture, to a temperature in the range of about 800° to about 1200° C., preferably in the vicinity of 1100° C. While the ore is held at such a temperature, it is intimately contacted with completely anhydrous HCl to chloridize the iron and manganese. In this particular form of the invention, the ore and chloridizing reagent may be moved in counter-current relationship through the reactor, if desired, the ore being continuously charged into the reactor at one end and the residue continuously removed from the other. Depending upon the efficiency of the contact between the chloridizing reagent and the ore, substantially all of its manganese and iron contents are converted to $MnCl_2$ and $FeCl_2$, respectively, in a period of from 1 to 3 hours or so, and these chlorides are sublimed at the reaction temperature. The chloridizing reactions may be represented by the formulae:

$$FeO+2HCl \rightarrow FeCl_2+H_2O$$
$$MnO+2HCl \rightarrow MnCl_2+H_2O$$

Any phosphorus present is also chloridized and sublimed, but other impurities such as silica and alumina remain unaffected in the ore residue left in the reactor so long as the chloridizing reaction is performed in the absence of carbon or other reducing agent.

In the accompanying flow diagram, the reactor is designated **1**, and a conduit for introducing the chloridizing reagent is designated **2**.

The sublimate gases from the chloridizing treatment are drawn off from the reactor as they accumulate and are conducted through a conduit 3 to a condenser 4, where the manganese and iron chlorides are condensed at a temperature in the range of about 350° to 650° C., while the phosphorus chloride, excess HCl, and water vapor pass through the condenser, as indicated by the arrows **5, 6**, to any suitable recovery system (not shown). The water formed by the reaction is efficiently removed with these gases, and the condensed manganese and iron chlorides are substantially completely anhydrous as deposited in the condenser.

The condensed chlorides may be temporarily stored out of contact with air for later electrolysis, or may be transferred directly into a molten bath of alkali metal chloride in an electrolytic cell 7 for electrolytic reduction.

The electrolytic cell is preferably of the character disclosed in my copending application Serial No. 201,089, filed December 16, 1950, for Methods of and Apparatus for Making Chromium (a continuation-in-part of an earlier application Serial No. 144,410, filed February 16, 1950), both said applications now being abandoned. In such a cell, a covered pot 8 of Inconel or other heat resistant alloy forms the cathode, the upper portion of the pot being offset outwardly at **9** to accommodate a suitable refractory **10**. An electrically non-conductive, highly inert magnesia refractory is preferred and may be mixed with water to form a suitable ramming mix, rammed in place, and dried to provide an inert, electrically non-

conductive surface 11 inside the pot for a substantial distance below the upper edge thereof entirely about its periphery.

The anode is a hollow rod or tube 15, preferably of graphite, that extends downwardly into the bath to adjacent the bottom of the pot so that it may also serve as a conduit for conducting hydrogen gas into the pot from a source 16 and discharging it into the bath 17 adjacent the bottom thereof, preferably in a downward direction. The hydrogen so discharged from the anode is dispersed and diffused throughout the bath, and particularly around the anode, for reaction with chlorine released from the anode during electrolysis of the manganese and iron chlorides. Hydrogen chloride resulting from reaction of hydrogen and chlorine in the cell, together with the excess hydrogen preferably supplied, accumulate in the cell above the bath and are withdrawn through a conduit 18 for temporary storage or for immediate reuse as described below.

The alkali metal chloride bath 17 employed in the electrolytic cell may be either sodium chloride, potassium chloride, or a mixture thereof in any desired proportions, and the bath is maintained at a temperature between about 650° and 1000° C., preferably between about 750° and 900° C. The bath level should be maintained above the lower edge of the refractory inner surface 11 of the pot at all times during electrolysis. Hydrogen is preferably introduced into the bath 17 through the anode 15 for sufficient time to saturate the bath and purge the space 19 above the bath of atmospheric gases to create a hydrogen atmosphere before the chlorides to be electrolyzed are introduced. The flow of hydrogen gas is continued as the chlorides to be electrolyzed are charged through the hydrogen atmosphere into the bath, thereby protecting these chlorides from oxidation.

The chlorides to be electrolyzed dissolve quickly in the bath 17 without fuming or foaming, and electrolysis is then carried out while continuing the flow of hydrogen into the bath from the anode 15. During electrolysis, the manganese and iron chlorides are disassociated, the manganese and iron being deposited as a ferromanganese alloy in fine granular form on the cathode walls of the pot, as shown at 20, and chlorine being released at the anode 15, where it is quickly converted to HCl by reaction with the hydrogen with which the bath is kept continuously saturated. The rapid conversion of the chlorine to HCl prevents reoxidation of the deposited manganese and iron back to chlorides and reduces the attack on the metal of the pot, which would tend to introduce other metal chlorides into the bath as impurities. The refractory surface 11 has also been found to be highly important in this connection, though the full explanation of its effect is obscure. The hydrogen apparently also assists in the reduction of the manganese and iron by chemical action while agitating the entire bath to maintain uniformity of its composition. These conditions permit the bath to be exhausted of iron and manganese by electrolysis and retard the formation of contaminants so that substantially no oxidizable chlorides or other impurities are entrained with the metal product when it is recovered from the cell. As a result, the deposited metal may be recovered with close to theoretical yields and better than 99% purity merely by decanting off the bath for reuse, scraping the alloy deposit from the walls of the pot, and washing the alloy with water to remove the soluble alkali chlorides entrained therewith.

The HCl withdrawn from above the bath through the conduit 18, together with excess hydrogen, is completely anhydrous and may be returned directly to the chloridizing reactor through the conduit 2 while adding only sufficient make-up chlorine from a source 22 to convert the excess hydrogen to HCl before the gases are introduced into the reactor. A source 23 of anhydrous HCl is also connected to the conduit 2 to supply all the HCl at the beginning of the process and any make-up required during the process.

Because of the great affinity of HCl for water, the excess HCl introduced into the reactor 1 during the chloridizing operation and withdrawn in gaseous form from the condenser 4 carries off all of the water vapor formed by the combination of hydrogen and oxygen in the reaction between HCl and the manganese and iron oxides. It is also mixed with a small amount of phosphorous chlorides sublimed from the reactor. This excess HCl may be reused to chloridize additional ore only after being thoroughly purified and dehydrated. Depending upon many variable factors, the recovery and reuse of this HCl may be uneconomical, and the excess HCl supplied to the reactor may be considered an inherent loss in such situations. The chlorine of the reacted HCl, however, is substantially entirely recovered from the electrolytic cell in the form of anhydrous HCl suitable for reintroduction directly into the reactor, as described above. Only sufficient chlorine need be added from the source 22 to take care of the excess hydrogen from the cell 7 and convert it to HCl, which serves in part to make up for losses from the condenser 4. Any additional make-up of HCl required may be supplied from the source 23.

By the simple and conventional expedient of providing standby condensers and electrolytic cells for connection into the system interchangeably with the condenser and electrolytic cell operating at any given time, and by feeding the ore and chloridizing gases continuously through the reactor in countercurrent fashion, the process may be made substantially continuous if desired.

The alloy product recovered from the electrolytic cell 7 is generally better than 99% pure with a carbon content less than one-tenth of one percent. The ratio of manganese to iron in the alloy is dependent upon, and substantially the same as, the ratio of manganese to iron in the ore charged into the chloridizing reactor, and the final recovery generally exceeds 90% of the original manganese and iron content of the ore.

In the event it should be desired to increase the ratio of manganese to iron in the final product, this is preferably done by substituting anhydrous chlorine for HCl at the beginning of the chloridizing reaction, whereby only the iron of the ore is chloridized to produce $FeCl_3$. This reaction is quite rapidly effected without subliming any manganese chloride at temperatures as low as 400° C. and up to about 650° or 700° C., temperatures in the range of about 500° to 600° being preferred, and the $FeCl_3$ sublimate may be condensed and recovered in a substantially pure anhydrous form. The treatment of the ore with chlorine may be continued until substantially all or any desired part of the iron content of the ore has been chloridized, sublimed, and collected. Thereupon, the flow of chlorine into the reactor is stopped and is replaced by anhydrous HCl while raising the temperature of the ore above about 800° C., preferably about 1100° C., for chloridizing the manganese and any remaining iron to $MnCl_2$ and $FeCl_2$, which are sublimed and may be deposited in a separate condenser.

An alternative, but less satisfactory, way in which a portion of the iron may be separately collected is to use a mixture of HCl and chlorine as the chloridizing reagent, whereby the chlorine converts some of the iron oxide to $FeCl_3$, which passes out of the reactor with the $FeCl_2$ and $MnCl_2$. A sharp separation of the $FeCl_3$ from the $FeCl_2$ and $MnCl_2$ may be effected by fractional condensation, using conventional equipment and techniques.

Treatment of steel slags

Slags from the open hearth process for the production of alloy steels are available in this country in substantial quantities and contain up to 11 or 12% manganese and 25 to 30% iron, along with substantial quantities of silicon dioxide, calcium oxide, aluminum oxide, magnesium oxide, and lesser amounts of phosphorus, carbon, and other

impurities. Since the ratio of manganese to iron in such slags is generally of the order of 1:3, their use as a source of manganese and iron for the production of ferromanganese makes it desirable to separate a substantial portion of the iron from the manganese as well as to separate the maganese and iron from the other impurities.

In the production of carbon-free ferromanganese from such slags in accordance with the present invention, the process steps are substantially identical with one of the alternative processes described above for the treatment of ores, in which anhydrous chlorine is first supplied to the reactor while holding the slag charge at a temperature well above 300° C. but below 700° C., preferably between about 500° and 600° C. This chloridizing reaction converts the iron oxide to ferric chloride, which is rapidly sublimed and condensed in a substantially pure, anhydrous form. While the slags contain small amounts of carbon up to about .3% or .4%, such amounts are insufficient to have any material effect as a reducing agent, and the reaction may be considered as being carried out in the substantial absence of a reducing agent. Under these conditions the silicon dioxide, aluminum oxide, calcium oxide, and magnesium oxide remain unaffected in the reactor. Substantially the only contaminant in the sublimate is phosphorus chloride, which is sufficiently volatile to be completely removed from the condenser in gaseous form along with the excess chlorine, small amounts of water vapor produced by the chloridizing reaction, and traces of carbon monoxide.

When the desired amount of iron in the starting material has been removed and condensed as $FeCl_3$, the flow of chlorine to the reactor is stopped and is replaced by anhydrous HCl, and the temperature of the charge in the reactor is raised to between about 800° and 1200° C., preferably in the vicinity of 1000° to 1100° C. As in the case of the treatment of oxide ores with this chloridizing reagent, the remaining iron and all of the manganese are chloridized to $FeCl_2$ and $MnCl_2$, respectviely, and are sublimed and condensed together in a substantially pure and completely anhydrous condition.

The mixed chlorides of iron and manganese are transferred to the electrolytic cell which is operated in the same manner as described above for the production of ferromanganese in a substantially pure, finely powdered condition. The separately condensed $FeCl_3$ may also be electrolyzed in the same type of electrolytic cell while employing the same fused alkali metal chloride bath to produce substantially pure iron in a finely powdered condition. By reason of the introduction of hydrogen gas in excess into the electrolytic cells in both cases, anhydrous HCl and the excess hydrogen are withdrawn from the cells during the electrolysis and may be reused in the second stage of the chloridizing reaction after adding only sufficient chlorine to react with the excess hydrogen.

By operating in this manner, better than 90% of the available iron and manganese in the slags is recoverable in the forms of substantially pure iron powder and substantially pure ferromanganese powder. In the event it is desired to completely separate the iron and manganese, the chloridizing treatment of the slag with chlorine gas may be continued until all of the iron content of the slag has been removed from the reactor as $FeCl_3$. The treatment of the residue in the reactor with anhydrous HCl then produces substantially pure $MnCl_2$ which may be sublimed and condensed separately from the iron. Electrolysis of the $MnCl_2$ in the same type of electrolytic cell and with the same bath ingredients and operating conditions produces substantially pure manganese in finely divided powdered form.

Treatment of high-carbon ferromanganese

The standard, high carbon ferromanganese of commerce generally contains about 78% to 82% manganese, around 7% carbon, up to 1% silicon dioxide, and the balance iron. It is produced both in lump form and in granular form, the latter being preferred for use in accordance with the present invention to produce carbon-free ferromanganese or to separate the iron and manganese with the production of substantially pure iron and manganese powders.

Depending upon the degree of separation of iron desired, if any, the process is carried out in the same manner as in the treatment of ores and slags. Chlorine is first used as the chloridizing reagent if separation of iron is desired, the chloridizing temperature preferably being between about 500° and 600° C. Otherwise, it is preferred that anhydrous HCl be used exclusively, in which case a temperature above 800° C. and preferably between 1000° and 1200° C. is employed. Alternatively, if desired, a mixture of chlorine and HCl may be employed at the latter temperature range, whereby a portion of the iron is sublimed as $FeCl_3$ and the remainder as $FeCl_2$ at the same time that the manganese is sublimed as $MnCl_2$. In this case, by reason of the greater volatility of the $FeCl_3$, fractional condensation is feasible to separate it in whole or in part from the $MnCl_2$ and $FeCl_2$.

The resulting chlorides, whether condensed separately or together, may be electrolyzed in the same manner as in the preceding examples to produce substantially pure, carbon free, iron powder, manganese powder, or ferromanganese powder with substantially the proportions of iron to manganese in the product as these metals are present in the chlorides charged to the electrolytic cell. About 90% recovery of the manganese and iron in the original high carbon ferromanganese may be obtained in commercial operations. Better than 99% pure manganese and iron powders and ferromanganese powders, containing as little as 0.05% carbon are readily produced.

From the foregoing description of the invention, it will be appreciated that the processes described are most flexible and may readily be varied in numerous respects to treat different raw materials with equal facility and efficiency. Accordingly, the invention is not intended to be limited to any particular processing conditions or the treatment or production of the specific materials mentioned for illustrative purposes except as required by the terms of the appended claims.

Having described my invention, I claim:

1. A process for recovering manganese values as anhydrous chloride from alloys and oxide ores containing manganese, iron, and other material, comprising contacting the material under anhydrous conditions in a reaction chamber at a temperature between about 315° C. and 700° C. with a chloridizing reagent consisting essentially of chlorine to convert at least a portion of the iron to ferric chloride and sublime the same, separating gaseous ferric chloride at it is formed, contacting the residue under anhydrous conditions in a reaction chamber at a temperature above about 800° C. with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride to convert the maganese to manganous chloride and any remaining iron to ferrous chloride and to sublime the same, and removing and condensing the second sublimate under anhydrous conditions, active oxidizing gases and active reducing gases being excluded from the reaction chamber during each of the chloridizing reactions.

2. A process for recovering manganese and iron values as manganese and iron chlorides from materials containing oxides of manganese, iron, and other metals, comprising heating said materials in a reaction chamber under anhydrous conditions to a temperature between about 400° and 700° C. while contacting said materials with a chloridizing reagent consisting essentially of anhydrous chlorine to form and sublime ferric chloride, active oxidizing gases other than chlorine and active reducing gases being excluded from the reaction chamber during the reaction therein, separating and condensing the sublimate containing ferric chloride under anhydrous conditions, substituting a chloridizing reagent consisting essentially of anhydrous hydrogen chloride for the chlo-

rine in said reaction chamber and raising the temperature therein to above about 800° C. to form and sublime manganese chloride while maintaining said anhydrous conditions, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the second reaction therein and separating and condensing the sublimate containing manganese chloride under anhydrous conditions.

3. A process for recovering manganese and iron values as $MnCl_2$ and $FeCl_2$ from alloys and oxide ores containing manganese, iron, and other materials, comprising heating the material containing the manganese and iron to a temperature above about 800° C. in a reaction chamber under anhydrous conditions, contacting said material in said chamber at said temperature with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride while excluding active oxidizing gases and active reducing gases from said reaction chamber to convert the manganese and iron to $MnCl_2$ and $FeCl_2$ and sublime the same, and removing the manganese and iron chloride sublimates as they are formed and condensing them under anhydrous conditions.

4. A process for producing substantially carbon-free $MnCl_2$ and $FeCl_2$ from high carbon ferromanganese, comprising heating the high carbon ferromanganese to a temperature above about 800° C. in a reaction chamber under anhydrous conditions, contacting the high carbon ferromanganese in said reaction chamber at said temperature with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride while excluding active oxidizing gases and active reducing gases from said reaction chamber to convert the iron and manganese to $MnCl_2$ and $FeCl_2$ and sublime the same, and removing the manganese and iron sublimates from the reaction chamber as they are formed and condensing them under anhydrous conditions.

5. The process of claim 1 in which said second sublimate is dissolved in a fused alkali metal chloride bath in a closed electrolytic cell and is electrolyzed while diffusing hydrogen gas through the bath to deposit manganese and any iron present at the cathode and release chlorine at the anode, whereby anhydrous hydrogen chloride is formed in the bath by reaction of hydrogen and chlorine, and removing anhydrous hydrogen chloride from the cell as it is formed and returning it to the process for treating additional residue from the first chloridizing reaction.

6. The process of claim 2 in which the condensed ferric chloride and the condensed manganese chloride are separately electrolyzed in fused alkali metal chloride baths in the presence of hydrogen gas diffused through the baths to deposit metal at the cathode and release chlorine for reaction with said hydrogen to form anhydrous hydrogen chloride, recovering the anhydrous hydrogen chloride from at least one of said baths and introducing it into said reaction chamber to form additional manganese chloride.

7. A process for recovering manganese values from alloys and oxide ores containing manganese, iron, and other material, comprising converting the manganese to manganese chloride by reaction under anhydrous conditions with a chloridizing agent selected from the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof, at a temperature sufficient to form and sublime manganese chloride, removing and condensing the sublimate under anhydrous conditions, electrolyzing the anhydrous condensate in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath to deposit the metal values of the condensate at the cathode and release chlorine for reaction with said hydrogen to form anhydrous hydrogen chloride, and recovering anhydrous hydrogen chloride from the bath and using it in the process in the conversion of additional manganese to manganese chloride while utilizing anhydrous hydrogen chloride as the sole chloridizing agent selected from said class, whereby any chlorine initially used in the process is recovered and reused in the form of anhydrous hydrogen chloride.

8. A process for recovering manganese values from alloys and oxide ores containing manganese, iron, and other material, comprising contacting the manganese-containing material under anhydrous conditions in a reaction chamber at a temperature above about 800° C. with a chloridizing reagent consisting essentially of a member of the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof, to form and sublime manganese chloride, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the reaction, separating and condensing the manganese chloride under anhydrous conditions as it sublimes, electrolyzing the separated manganese chloride in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath, whereby manganese is deposited at the cathode and chlorine is released at the anode and reacted with hydrogen to form anhydrous hydrogen chloride, and recovering anhydrous hydrogen chloride from the bath and introducing it into said reaction chamber to form additional manganese chloride.

9. A process for recovering manganese values from alloys and oxide ores containing manganese, iron, and other material, comprising contacting the manganese-containing material under anhydrous conditions in a reaction chamber at a temperature above about 800° C. with a chloridizing reagent consisting essentially of a member of the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof, to form and sublime manganese chloride, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the reaction, separating and condensing the manganese chloride under anhydrous conditions as it sublimes, dissolving the condensed manganese chloride in a fused alkali metal chloride bath in a closed electrolytic cell and electrolyzing said bath while diffusing hydrogen gas therethrough to deposit manganese at the cathode and release chlorine at the anode, whereby anhydrous hydrogen chloride is formed in the bath by reaction of hydrogen and chlorine, and removing anhydrous hydrogen chloride from the cell as it is formed and introducing it into said reaction chamber to form additional manganese chloride.

10. A process for recovering manganese values from alloys and oxide ores containing manganese, iron, and other material, comprising contacting the material under anhydrous conditions in a reaction chamber at a temperature between about 400° and 650° C. with a chloridizing reagent consisting essentially of chlorine to convert a portion of the iron to ferric chloride and sublime the same, separating gaseous ferric chloride as it is formed, contacting the residue under anhydrous conditions in a reaction chamber at a temperature above about 800° C. with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride to convert the manganese to manganous chloride and the remaining iron to ferrous chloride and to sublime the same, and removing and condensing the second sublimate under anhydrous conditions, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the reaction, separately electrolyzing the two condensates in fused alkali metal chloride baths in closed electrolytic cells while diffusing hydrogen through the baths to deposit iron powder at the cathode in one case and ferromanganese powder at the cathode in the other case while releasing chlorine into the bath at the anode in both cases, whereby anhydrous hydrogen chloride is formed in the baths by reaction of hydrogen and chlorine, removing anhydrous hydrogen chloride from the baths as it is formed and returning it to the process for use in

the second chloridizing step, and recovering substantially pure iron powder from one bath and substantially pure ferromanganese powder from the other.

11. A process for recovering manganese values from materials containing oxides of manganese and other metals, comprising converting the manganese of the oxides to manganese chloride by reaction under anhydrous conditions in a reaction chamber at a temperature above about 800° C. with a chloridizing reagent consisting essentially of a member of the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof, to form and sublime manganese chloride, active oxidizing gases other than chlorine and active reducing gases being excluded from the reaction chamber during the reaction, separating and condensing the manganese chloride under anhydrous conditions as it sublimes, electrolyzing the separated manganese chloride in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath to deposit manganese and release chlorine for reaction with said hydrogen to form anhydrous hydrogen chloride, and recovering anhydrous hydrogen chloride from the bath and using it in the process in treating said materials while utilizing anhydrous hydrogen chloride as the sole chloridizing agent selected from said class, whereby any chlorine initially used in the process is recovered and reused in the form of anhydrous hydrogen chloride.

12. A process for recovering manganese values from materials containing oxides of manganese and other metals, comprising heating said materials in a reaction chamber under anhydrous conditions to a temperature above about 800° C. while contacting them with a chloridizing reagent consisting essentially of a member of the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof to form and sublime manganese chloride, active oxidizing gases other than chlorine and active reducing gases being excluded from the reaction chamber during the reaction, removing and condensing the manganese chloride under anhydrous conditions as it sublimes, electrolyzing the condensed manganese chloride in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath, whereby manganese is deposited at the cathode and chlorine is released at the anode and reacted with hydrogen to form anhydrous hydrogen chloride, and recovering anhydrous hydrogen chloride from the bath and introducing it into said reaction chamber to form additional manganese chloride.

13. A process for treating materials containing oxides of manganese, iron and other metals, comprising heating said materials in a reaction chamber under anhydrous conditions to a temperature above about 800° C. while contacting them with a chloridizing reagent consisting essentially of a member of the class consisting of anhydrous chlorine, anhydrous hydrogen chloride, and mixtures thereof to form and sublime a mixture of manganese and iron chlorides, active oxidizing gases other than chlorine and active reducing gases being excluded from the reaction chamber during the reaction, removing the mixture of manganese and iron chlorides from the reaction chamber as they sublime and condensing them under anhydrous conditions as mixed chlorides, electrolyzing the manganese and iron chlorides in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath to deposit manganese and iron at the cathode and release chlorine at the anode for reaction with said hydrogen to form anhydrous hydrogen chloride, recovering anhydrous hydrogen chloride from said bath and introducing it into said reaction chamber to form additional manganese and iron chlorides.

14. A process for recovering manganese and iron values from materials containing oxides of manganese, iron, and other metals, comprising heating said materials in a reaction chamber under anhydrous conditions to a temperature between about 400° and 700° C. while contacting said materials with a chloridizing reagent consisting essentially of anhydrous chlorine until at least a portion of the iron content is converted to gaseous ferric chloride, active oxidizing gases other than chlorine and active reducing gases being excluded from said reaction chamber during the reaction therein, removing the gaseous ferric chloride as it is formed, substituting a chloridizing reagent consisting essentially of anhydrous hydrogen chloride for the chlorine in said reaction chamber while maintaining said anhydrous conditions and raising the temperature in the chamber above about 800° C. to convert the manganese content and any remaining iron content to gaseous manganese and ferrous chlorides, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the second reaction therein, removing and condensing the latter chlorides together under anhydrous conditions as a mixture, electrolyzing said mixture of chlorides in a fused alkali metal chloride bath in the presence of hydrogen gas diffused through the bath to deposit manganese and iron at the cathode and release chlorine at the anode for reaction with said hydrogen to form anhydrous hydrogen chloride, and recovering anhydrous hydrogen chloride from the bath and introducing it into said reaction chamber for chloridizing additional manganese and iron.

15. A process for recovering manganese values from alloys and oxide ores containing manganese, iron, and other material, comprising chloridizing the manganese containing material under anhydrous conditions at a temperature above about 800° C. in a reaction chamber with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride to convert at least the manganese content thereof to manganese chloride and sublime the same, active oxidizing gases and active reducing gases being excluded from the reaction chamber during the chloridizing reaction, removing and condensing the sublimate under anhydrous conditions, dissolving the condensate in a fused alkali metal chloride bath, electrolyzing said bath while diffusing hydrogen therethrough to deposit manganese and release chlorine in the bath, whereby anhydrous hydrogen chloride is formed in the bath by reaction of hydrogen and chlorine, removing hydrogen chloride from the bath as it is formed, and returning the hydrogen chloride to the process for use as a chloridizing reagent in chloridizing additional manganese-containing material.

16. A process for recovering substantially carbon-free ferromanganese from high carbon ferromanganese, comprising reacting the high carbon ferromanganese in a reaction chamber with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride at a temperature above about 800° C. under anhydrous conditions to produce and sublime maganese and iron chlorides, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the reaction, removing and condensing said chlorides under anhydrous conditions, electrolyzing said chlorides in a fused alkali metal chloride bath while diffusing hydrogen through the bath to deposit carbon-free ferromanganese and release chlorine in the bath, whereby anhydrous hydrogen chloride is produced in the bath by reaction of hydrogen and chlorine, and removing anhydrous hydrogen chloride from the bath as it is formed and returning it to the process for chloridizing additional high carbon ferromanganese.

17. A process for recovering substantially carbon-free ferromanganese from high carbon ferromanganese, comprising heating the high carbon ferromanganese in a reaction chamber under anhydrous conditions to a temperature above about 800° C. while contacting it with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride to form and sublime manganese and iron chlorides, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the reaction, and removing and condensing the manganese

and iron chlorides under anhydrous conditions as they sublime, dissolving the condensed manganese and iron chlorides in a fused alkali metal chloride bath in a closed electrolytic cell and electrolyzing said bath while diffusing hydrogen therethrough to deposit substantially carbon-free ferromanganese at the cathode and release chlorine at the anode, whereby anhydrous hydrogen chloride is formed in the bath by reaction of hydrogen and chlorine, removing anhydrous hydrogen chloride from the cell as it is formed and introducing it into said reaction chamber to chloridize additional high carbon ferromanganese, and recovering substantially carbon-free ferromanganese from said bath.

18. A process for recovering substantially carbon-free manganese from high carbon ferromanganese, comprising chloridizing high carbon ferromanganese in a reaction chamber under anhydrous conditions at a temperature between about 500° and 600° C. with a chloridizing reagent consisting essentially of anhydrous chlorine to form and sublime ferric chloride, active oxidizing gases other than chlorine and active reducing gases being excluded from the reaction chamber during said chloridizing reaction, and removing the ferric chloride sublimate as it forms until substantially all of the iron has been separated from the high carbon ferromanganese, chloridizing the residue in said reaction chamber under anhydrous conditions at a temperature in the range from about 800° to 1200° C. with a chloridizing reagent consisting essentially of anhydrous hydrogen chloride to form and sublime manganese chloride, active oxidizing gases and active reducing gases being excluded from said reaction chamber during the second of chloridizing reactions, and removing and condensing the manganese chloride sublimate under anhydrous conditions as it forms, dissolving the condensed manganese chloride in a fused alkali metal chloride bath in a closed electrolytic cell and electrolyzing said bath while diffusing hydrogen therethrough to deposit manganese at the cathode and release chlorine at the anode, whereby anhydrous hydrogen chloride is formed in the bath by reaction of hydrogen and chlorine, and removing anhydrous hydrogen chloride from the cell as it is formed and returning it to the process for treating additional residue from the first chloridizing reaction.

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