June 26, 1956 H. S. COOPER 2,752,301

RECOVERY OF CHROMIUM AND IRON VALVES FROM CHROMIUM-IRON ORES

Filed March 7, 1951 2 Sheets-Sheet 1

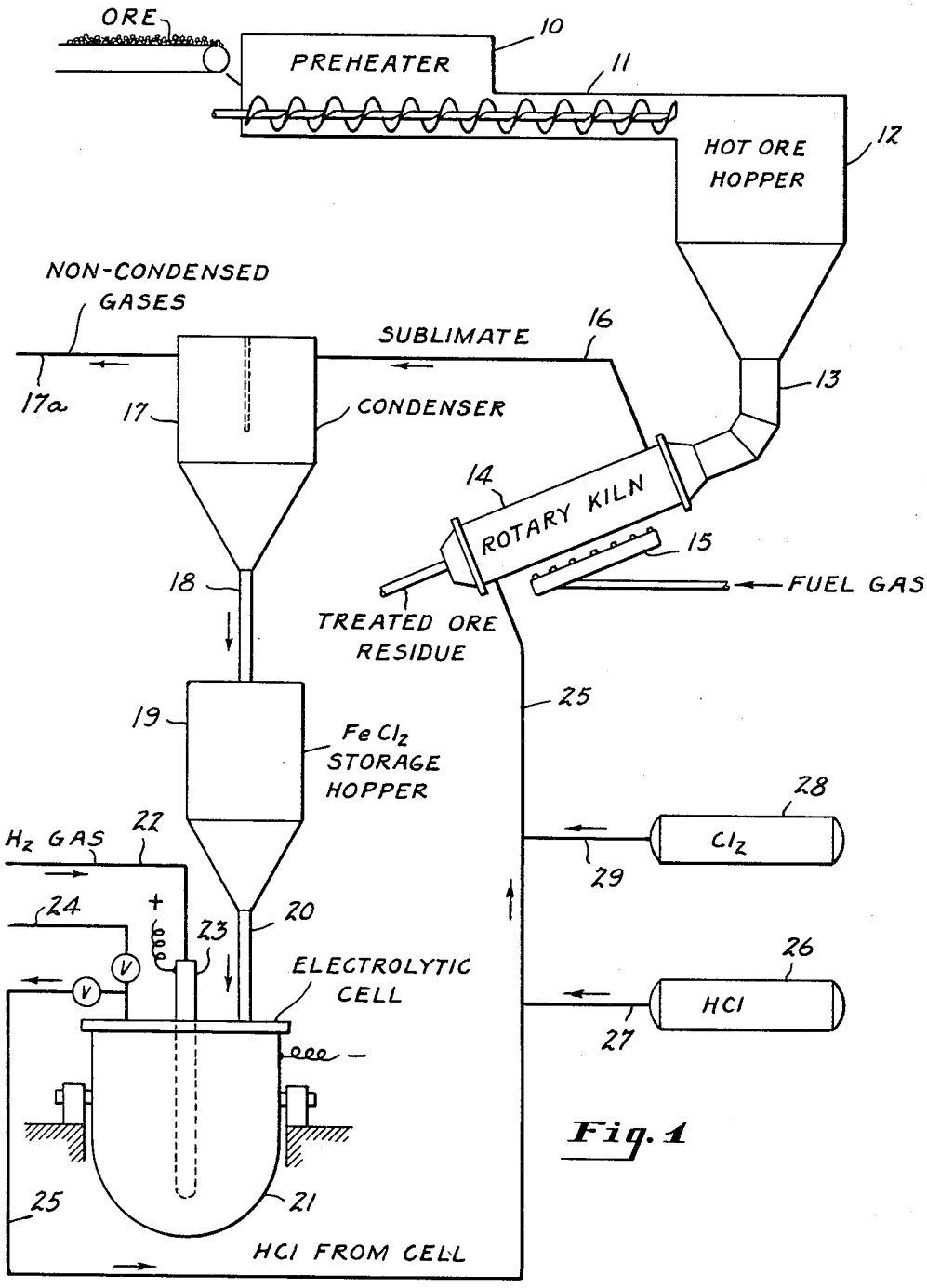


Fig. 1

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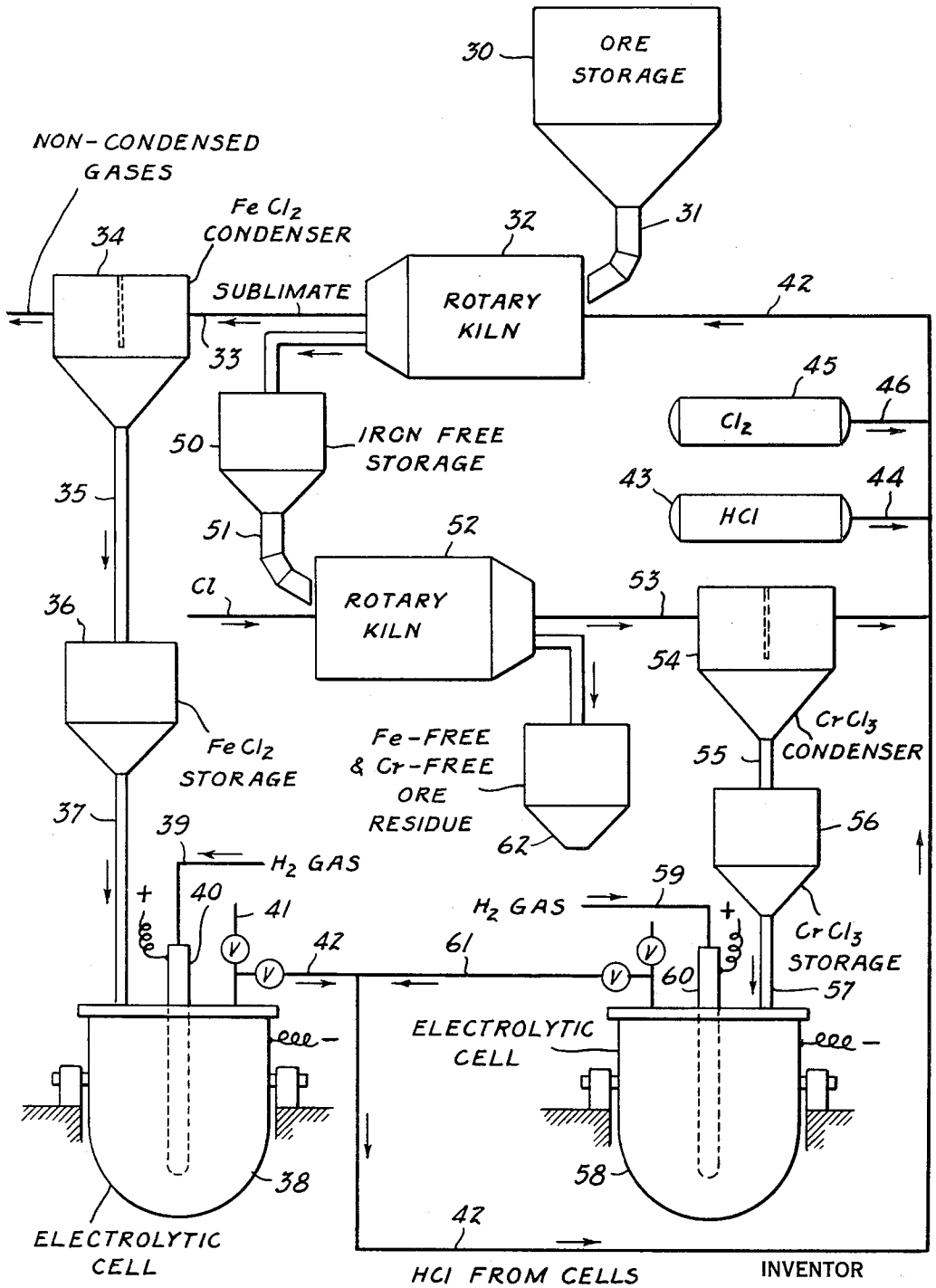


Fig. 2

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2,752,301

RECOVERY OF CHROMIUM AND IRON VALUES FROM CHROMIUM-IRON ORES

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Application March 7, 1951, Serial No. 214,247

22 Claims. (Cl. 204—10)

This application relates to the treatment of chromium ores and particularly to the treatment of chromite ores for selectively separating desired constituents therefrom.

A major portion of the chromium used by industry today goes into steels as an alloying element, though there is also a large demand for chromium metal in a pure form for other purposes, and also for pure chromium salts for use in the chemical industries. The principal source of chromium is the ore known as "chromite," which consists principally of chromium and iron oxides in admixture with various other minerals. Though much of the chromium oxide and iron oxide contents of chromite ores are combined in the form of ferrous chromite ($Cr_2O_3 \cdot FeO$), for most purposes the chromium and iron may be considered as being practically all in the form of Cr_2O_3 and FeO, respectively. Depending on their source, chromite ores generally contain about 30 to 55% chromic oxide, about 10 to 25% ferrous oxide, with widely varying chromium-iron ratios calculated on a metallic basis, and other minerals consisting largely of oxides of magnesium, aluminum, silicon, and calcium in various proportions and combinations. When used to produce pure chromium metal or pure chromium salts, chromite ore has been handled in various ways, but the principal problem has always been the elimination of the iron oxide and other mineral impurities at some stage in the process.

When used for the production of chromium steels, the chromite ores are generally first concentrated and smelted to eliminate most of the components other than chrominum and iron and to produce a ferro-chromium master alloy of one of the following two commercial grades;

1. High carbon—66 to 70% Cr, 4.5 to 7% C, balance largely Fe
2. Low carbon—66 to 70% Cr, 0.03 to 2% C, balance largely Fe

The high carbon master alloy is made by smelting the ore with excess carbon. The low carbon master alloy is usually made by smelting with excess silicon as the reducing agent. These master alloys are added to steels in the required amounts to produce the desired chromium contents in the final chromium steels.

For simple, low chromium steels, the high carbon ferro-chromium may be employed without introducing excessive amounts of carbon. The high chromium and complex chromium steels, however, especially those containing nickel, must generally be low in carbon content and, therefore, require the use of low carbon ferro-chromium.

Because the iron in the ferro-chromium master alloy also forms a part of the final product, the ratio of chromium to iron in the master alloy is important. The presence of too much iron in the master alloy requires the use of excessive amounts to obtain the desired chromium content in the final product, thus exerting a deleterious chilling effect on the melt. Moreover, the use of such high-iron master alloys would be uneconomical.

Depending on their source, the chromite ores generally contain about 30 to 55% chromic oxide and about 10 to 25% ferrous oxide with widely varying chromium-iron ratios. Most of the ores fall roughly into one of the following three commercial classes:

1. Refractory grade—30 to 40% Cr_2O_3 and 13 to 25% FeO
2. Chemical or intermediate grade—40 to 45% Cr_2O_3 and 18 to 25% FeO
3. Metallurgical grade—45 to 55% Cr_2O_3 and 10 to 15% FeO

Thus, for practically all metallurgical uses, only the metallurgical grades of chromite contain a sufficiently high chromium-iron ratio to produce a practically useful ferro-chromium master alloy. To be used for producing a satisfactory ferro-chromium master alloy, the leaner grades of chromite must be treated in some manner to increase the chromium-iron ratio by eliminating a portion of the iron. This has heretofore been so difficult and expensive as to effectively preclude any significant metallurgical use of either of the two leaner grades of chromite.

Unfortunately, many of the deposits of chromite throughout the world are of the low grade (refractory or chemical) varieties which have been economically unsuitable for metallurgical uses. Many countries, including the U. S., depend almost entirely on foreign sources for their supplies of the metallurgical grades of chromite which are in such great demand, though many of these same countries, again including the U. S., have extensive deposits of lower grade chromite ores. As a consequence, there has been an important, widespread, and long recognized need for a practical and economical process for beneficiating the lower grades of chromite ore to increase the chromium-iron ratio. Under the present unsettled world conditions, the necessity for avoiding reliance upon foreign sources of such critical raw materials has rendered solution of the chromite beneficiation problem even more urgent.

While this problem has been the subject of extensive investigation, particularly during the last two decades, and various types of ore treatment have been tried, the most promising processes have involved some kind of chloridizing of the ore with removal of volatile metal chlorides as gases or vapors. In some cases fractional condensation of the gases or vapors has been employed to effect further separation of the various volatilized chlorides.

Numerous patents have been granted on processes of this general character and on apparatus for carrying out such processes. In some cases the inventions have been directed to the formation and vapor phase removal of only the chlorides of iron and chromium, followed by fractional condensation. In other cases, chlorides of other metals have also been formed and vaporized in substantial quantity, requiring more complex fractional condensation operations. In still other cases, efforts have been made to vaporize and condense chlorides of the iron only. In spite of the great need for practical processes of this character, however, their general use on a commercial scale has heretofore been found to be impractical.

One of the major objections to the prior art processes has been that the chlorination and vaporization operations have not been sufficiently selective or complete, and sufficiently selective fractional condensation has been accomplished only at prohibitive costs.

Another major objection to the prior art processes has been the difficulty of obtaining efficient chloridization where the temperatures, apparatus, and reactants employed have been chosen to render the chloridization more selective. The less volatile chlorides of calcium and magnesium vaporize only at excessively high temperatures and normally remain in the reactor in a fused or semi-

fused condition, coating the ore and choking the reactor with a gas impervious mass. This both slows down the reaction and makes it difficult to carry it to completion.

The chloridizing agents most frequently mentioned in the prior art as equivalent chloridizing agents have included chlorine gas, hydrochloric acid, phosgene, sulfur tetrachloride, and ferric chloride. The ore has generally been mixed with various amounts of carbon to aid in the reduction of the metal oxides to render them more readily or more selectively attacked by the chloridizing agents. Various temperatures have been maintained by various expedients for controlling the reactions. Special forms of reactors have been employed to facilitate the reactions. And numerous vapor collection and condensation devices and procedures have been employed to improve the selectivity of the fractional condensation. However, none of these devices or expedients has been sufficiently successful to permit the large scale treatment of low grade chromite ores for general use in place of the naturally occurring, but relatively scarce, ores of metallurgical grade.

Accordingly, the principal object of the present invention is to provide a process for chloridizing low grade chromite ores that is sufficiently selective to effect the separation of iron and chromium values without fractional condensation.

A related and more specific object of the invention is to provide a chloridizing process that selectively chloridizes and removes only the iron component of chromite ores.

A further object of the invention is to provide a process for treating chromite ores to selectively remove all or any desired part of the iron component.

Another related and more specific object of the invention is to provide a chloridizing process for producing from chromite ores a pure, anhydrous, ferrous chloride suitable for direct electrolysis to produce pure iron powder.

A further object of the invention is to provide a chloridizing process for producing from chromite ores a substantially pure, anhydrous chromium chloride suitable for direct electrolysis to produce pure chromium powder.

A further object of the invention is to provide a chloridizing process for producing from chromite ores a substantially pure, anhydrous mixture of ferric and chromic chlorides in selected proportions suitable for direct electrolysis to produce a pure ferro-chromium alloy.

Still another object of the invention is to provide a system for treating chromite that may be readily controlled to selectively separate all or any desired proportion of the iron component and all or any desired proportion of the chromium component.

Still another object of the invention is to provide a system for chloridizing chromite to produce in substantially pure, anhydrous form, ferrous chloride and either chromic chloride or a mixture of ferric and chromic chlorides suitable for direct electrolysis to produce substantially pure metallic iron and metallic chromium or a ferro-chromium alloy.

Still another object of the invention is to provide a system for chloridizing chromite ores, that includes suitable electrolytic cells for respectively producing metallic iron and metallic chromium or a ferro-chromium alloy by the fused bath electrolysis of chlorides formed in the system, with the recovery of gases from the electrolytic cells for use in chloridizing additional ore.

A general object is to accomplish the foregoing objectives in a simple and economical manner suitable for the large scale treatment of chromite ores, particularly those of the lower grade.

One important feature of the invention involves the use of dry, substantially pure, hydrogen chloride gas as a first chloridizing agent in the presence of less than the customary amount of carbon or, preferably, no carbon at all. At temperatures above about 850° C., up to and including temperatures as high as 1100° C., or more, in the absence of carbon, dry hydrogen chloride attacks only the iron oxide component of chromite ores, converting the iron to ferrous chloride which volatilizes rapidly

above about 900° C. The reaction is represented by the formula—

$$Cr_2O_3 \cdot FeO + 2HCl \rightarrow FeCl_2 + H_2O + Cr_2O_3$$

So long as any carbon present does not exceed a roughly critical limit that is related to the amount of ferrous oxide present, as more fully explained hereinafter, it has no appreciable effect on the reaction and, at most, only insignificant amounts of chlorides of metals other than iron are formed.

The completeness of removal of the iron is controllable by varying the conditions of the dry hydrogen chloride treatment, leaving as the residue a beneficiated chromite containing any desired chromium-iron ratio, including a substantially completely iron-free residue wnen desired. By reason of the high selectivity and the high temperature of the treatment, the condensed $FeCl_2$ is substantially 100% pure and anhydrous, which renders it ideally suited for fused bath electrolysis to produce high purity iron powder.

Another important feature of the invention involves the fused bath electrolysis of the $FeCl_2$ in a bath of alkali metal chloride permeated with hydrogen gas, depositing elemental iron on the cathode and releasing chlorine from the anode. The chlorine combines in the bath with the hydrogen to produce dry hydrogen chloride suitable for return to the first chloridizing reactor for use as the chloridizing agent.

Another optional, but important feature of the invention involves carrying out the first chloridizing reaction in the complete absence of carbon until the iron is substantially completely removed, then subjecting the iron-free residue to a second chloridizing treatment with straight chlorine gas above about 850° C., up to and including temperatures as high as 1100° C., in the presence of an amount of carbon just sufficient to react with the oxygen of the Cr_2O_3 component to form carbon monoxide. This treatment chloridizes the chromium, which is removable as chromium chloride vapor, with substantially no contamination by chlorides of any of the undesired gangue material. A substantially pure and anhydrous chromium chloride results from condensation of the removed vapors. The reaction is represented by the formula—

$$Cr_2O_3 + 3C + 3Cl_2 \rightarrow 2CrCl_3 + 3CO$$

When employing this optional operation to produce chromium chloride, another important feature of the invention involves electrolysis of the chromium chloride in a fused alkali metal chloride bath of the same type employed for $FeCl_2$ and with hydrogen gas permeating the bath to produce elemental chromium of high purity and additional dry hydrogen chloride for return to the first chloridizing reactor.

Still another optional and important feature of the invention involves carrying out the first chloridizing reaction to remove sufficient iron to produce a residue having a predetermined chromium: iron ratio, then subjecting the residue with a reduced iron content to a second chloridizing treatment above about 850° C., up to and including temperatures as high as 1100° C., in the presence of an amount of carbon just sufficient to react with the oxygen of the oxides in both iron and chromium in the residue to form carbon monoxide. This treatment chloridizes both the chromium and the remaining iron which are removed as chromic and ferric chloride vapors substantially free from contamination by chlorides of any of the undesired gangue materials. Upon condensation of these vapors, a substantially pure, carbon-free, anhydrous mixture of solid chromic and ferric chlorides in the same proportions (based on metallic content) as the proportions of the metals in the iron impoverished residue from the first chloridizing treatment is obtained. When the mixed chlorides are electrolyzed in a fused alkali metal chloride bath of the same type mentioned above and with hydrogen gas permeating the bath, a substantially carbon-free ferro-chromium alloy is recovered from

the cathode in fine crystalline form and dry hydrogen chloride is recovered for return to the first chloridizing reactor.

The first chloridizing reaction and the fused bath electrolysis of $FeCl_2$ are thus carried out in a closed system as a result of the reconversion of chlorine to HCl and return of the HCl to the chloridizing reaction. Employment of the second chloridizing reaction and the fused bath electrolysis of $CrCl_3$ or mixed chromic and ferric chlorides contributes additional dry HCl for use in the first chloridizing reaction, thus further improving the economy of the entire process.

The foregoing and various additional objects, features, and advantages of the invention will be more fully understood from the following detailed description of two alternative ore treatment systems and from the accompanying drawings in which—

Figure 1 is a flow diagram of a system for treating ore to remove a portion of the iron content, producing an iron impoverished ore residue and substantially pure metallic iron powder as the final products; and

Figure 2 is a flow diagram of a system for treating ore in which the iron content of the ore is first substantially completely removed in the form of ferrous chloride, and the chromium content of the ore is then substantially completely removed in the form of $CrCl_3$, the iron and chromium chlorides then being separately disassociated in electrolytic cells for the production of substantially pure elemental iron powder in one cell and substantially pure elemental chromium powder in the other cell.

In both Fig. 1 and Fig. 2 of the drawings, the individual pieces of apparatus are represented diagrammatically, only sufficient structural detail being shown in a few instances to indicate the general nature of preferred types of apparatus.

Referring first to Figure 1, the system shown therein for illustrative purposes comprises any suitable furnace **10** for preheating the ore to be treated in the system; a conveyor **11**, which may be of the rotating screw type for feeding preheated ore from the furnace **10** to a hot ore storage hopper **12**; a conduit or suitable conveyor **13** for feeding ore at a desired rate from the hopper **12** to a reactor **14**, which may be in the form of an inclined, rotatable, tube-type kiln externally heated by a gas burner **15** or the like; a suitable conduit **16** for removing gaseous reaction products from the reactor **14** and transporting them to a condenser **17**; a suitable conduit or conveyor **18** for transporting solid material from the condenser **17** to a temporary storage hopper **19**; a conduit or suitable conveyor **20** for feeding solid material from the storage hopper **19** into a closed electrolytic cell **21**; a hydrogen gas supply conduit **22** for supplying hydrogen gas to the electrolytic cell **21**, preferably through a hollow graphite anode **23** and into the cell adjacent the bottom thereof; a valve-controlled blow-off conduit **24** for diverting gases emerging from the electrolytic cell during a preliminary scavenging operation; a valve-controlled conduit **25** for removing gases released within the electrolytic cell during electrolysis and conveying them back to the reactor **14**; a source **26** of hydrogen chloride connected to the conduit **25** through a branch conduit **27** for supplying additional hydrogen chloride to the system as needed; and, if desired, a source **28** of chlorine connected to the conduit **25** through a branch conduit **29** for supplying sufficient chlorine to react with at least part of the excess hydrogen normally exhausted from the electrolytic cell **21** in admixture with hydrogen chloride.

The hot ore hopper **12** in the type of system illustrated in Fig. 1 is intended merely to provide a temporary storage for receiving preheated ore continuously or intermittently at any desired rate from the furnace **10** and supplying it continuously or intermittently at a desired rate to the reactor **14**, the hopper being suitably insulated to perform this function with a minimum of heat loss.

The reactor **14** may be of any suitable design for receiving solid, granular material at its upper end and tumbling slowly through the reactor and out the opposite lower end, while a gas reagent, admitted adjacent the lower end of the reactor, flows counter-current therethrough and reacts with the granular material to produce gaseous reaction products withdrawn adjacent the upper end of the reactor through the conduit **16**.

The condenser **17** may be of any conventional type commercially employed in the art, and is preferably so located as to receive the gaseous products from the reactor **14** after a minimum travel through the conduit **16**. As nearly as physically possible, the reactor **14** should exhaust gaseous products directly into the condenser **17**, where heat is extracted therefrom to condense them to solid form. The noncondensed gases, including excess HCl, water vapor, and, in some cases, substantial amounts of H_2, are drawn off as indicated by the arrow **17***a*.

The storage hopper **19**, like the hopper **12**, merely serves to receive solid material continuously or intermittently at a desired rate from one piece of apparatus (the condenser **17**) and to feed the solid material continuously or intermittently at a desired rate to another piece of apparatus (the electrolytic cell **21**).

The electrolytic cell **21** is preferably of the general character disclosed in my copending applications Serial No. 144,410, filed February 16, 1950 (now abandoned), Serial No. 201,089, filed December 16, 1950 (now abandoned), and Serial No. 453,898, filed September 2, 1954. In such a cell, a closed metal pot forms the cathode, and the anode **23** is a hollow rod or tube, preferably of graphite, that extends downwardly to adjacent the bottom of the pot and serves as a conduit for conducting hydrogen gas into the pot and discharging it into the contents of the pot adjacent the bottom thereof, whereby the gas is dispersed and diffused throughout the contents of the pot for reaction with chlorine released from the anode during electrolysis. The hydrogen chloride resulting from direct combination of hydrogen and chlorine in the electrolytic cell, together with the excess hydrogen desirably supplied to the cell, are exhausted through the top of the cell and carried off by the conduit **25**, as pointed out above.

In accordance with the invention, a finely granulated ore containing chromium and iron oxides, such as chromite, is introduced into the furnace; heated to a temperature preferably in the range of about 1200° to 1300° C.; collected in the hopper **12**; and discharged as needed through the conduit or conveyor **13** into the upper end of the reactor **14** at a temperature not greatly below that at which it emerged from the furnace **10** and preferably above about 1000° C. During passage of the ore through the reactor **14** it is maintained at a temperature of at least 850° C. and preferably between about 900° and 1050° C., and the gas burner **15** is used for supplying additional heat for this purpose as required.

During passage of the ore in a state of agitation through the reactor **14**, it is intimately contacted by dry hydrogen chloride supplied at the lower end of the reactor and flowing upwardly and counter-current to the direction of the movement of the ore. The dry HCl readily reacts with the ferrous oxide in the ore, converting it to ferrous chloride, which is removed from the upper end of the reactor through the conduit **16** along with the excess HCl that is preferably supplied to the reactor. In the absence of an excessive amount of carbon, the dry HCl is highly selective in its action and does not attack the oxides of chromium, magnesium, aluminum, calcium, and silicon that, along with ferrous oxide, constitute practically all of most chromite ores. Therefore, the ore residue exhausted from the lower end of the reactor may contain a readily controllable fraction only of the original iron content of the ore, depending upon

(*a*) The rate at which the ore is supplied to the reactor,
(*b*) The fineness of the ore particles
(*c*) The rate at which dry HCl is supplied to the reactor,

(*d*) The time interval during which the ore travels from one end of the reactor to the other,

(*e*) The violence of the agitation of the ore during its travel through the reactor, and

(*f*) The temperature maintained in the reactor.

By a proper control of the variables mentioned, the percentage of iron removed may be regulated over a wide range from a relatively small percentage to a figure closely approaching 100% of the iron in the ore.

The amount of free carbon that may be tolerated with the ore during the treatment with hydrogen chloride, for reasons not fully understood, may be related roughly to the amount of oxygen present in the form of iron oxide in the ore residue. So long as the free carbon present at any stage during the HCl treatment does not materially exceed that amount which, if combined with the oxygen of the residual iron oxide, would form carbon monoxide, none of the chromium appears to be affected by the HCl. In the presence of a materially greater quantity of free carbon, chromic chloride is formed and vaporized in greater and greater amounts as the carbon:iron oxide ratio in the residual ore is raised by removal of iron oxide. In the presence of an original amount of carbon less than the limiting equivalency indicated, only ferrous chloride is formed and sublimed and the carbon, which does not enter into this reaction, also seems to remain unaffected. When the amount of iron oxide in the residual ore has been reduced in this manner, the carbon:iron oxide ratio is correspondingly increased. When this ratio materially exceeds the limiting equivalency indicated, chromic chloride begins to be formed and sublimes with the ferrous chloride.

Thus, to avoid contamination of the ferrous chloride sublimate with chromic chloride, the amount of carbon originally present should be sufficiently small so that the carbon:iron oxide ratio in the sublimate at the end of the HCl treatment is not substantially greater than the limiting ratio explained above. If all of the iron is to be removed as ferrous chloride, the carbon:iron oxide ratio in the original charge must be substantially zero. If a portion of the iron oxide is to be left in the residual ore, an amount of carbon based on that amount of iron oxide may be tolerated in the original charge.

The ferrous chloride removed from the reactor through the conduit **16** is readily condensed in the condenser **17** at a temperature in the range of about 350° to 650° C. without condensing the water vapor formed with the $FeCl_2$ in the reactor. The water vapor, along with the excess HCl introduced into the reactor, are removed from the condenser **17** as indicated at **17***a*. The intense affinity of HCl for H_2O apparently assists in preventing hydration of the $FeCl_2$ and insuring substantially complete removal of the H_2O from the system. This HCl and H_2O mixture must be carefully and thoroughly dehydrated if the HCl is to be reused for the treatment of additional ore. This requires the use of special apparatus and techniques forming no part of the present invention and, therefore, not shown or described herein. By reason of the highly selective action of the dry HCl in the reactor **14**, the gaseous $FeCl_2$ removed from the reactor is normally better than 99% pure, and solid $FeCl_2$ of substantially the same purity is recovered from the condenser and temporarily stored in the hopper **19** for use as needed in the electrolytic cell **21**. Because of the nature of the process by which the $FeCl_2$ is made and condensed, it is substantially completely anhydrous and, therefore, ideally adapted to be used as a source of iron in a fused bath electrolysis process. It is also highly significant that the sublimate is in the form of $FeCl_2$ rather than $FeCl_3$, since less power is required in the electrolytic cell to reduce the iron from its lower state of oxidation.

The electrolysis process, as carried out in the electrolytic cell **21**, involves essentially the following operations: a fused bath of sodium chloride, potassium chloride, or a mixture thereof in any desired proportion, is first prepared and brought to a temperature between about 650° and 1000° C., the preferred temperature being between 750° and 900° C. After forcing hydrogen gas downwardly through the fused alkali metal chloride bath for a sufficient time to saturate the bath with hydrogen and to scavenge all air from the space above the bath and blowing it off through the branch conduit **25**, a charge of $FeCl_2$ is introduced into the bath through the hydrogen atmosphere to protect it from oxidation. The $FeCl_2$ dissolves quickly in the bath without fuming or foaming, and electrolysis is then begun by connecting the terminals of the cell to a source of direct current power. The introduction of hydrogen gas into the bath is continued throughout the electrolytic process to keep the bath saturated with an excess of hydrogen, whereby the chlorine of the $FeCl_2$, released at the anode, is quickly converted to HCl and is exhausted in that form through the conduit **25** for return to the reactor **14**. The hydrogen also seems to have a tendency to reduce part of the $FeCl_2$ chemically, thus improving the apparent electrical efficiency of the process.

At the conclusion of the electrolysis operation, which may be carried substantially to completion, the flow of hydrogen gas through the conduit **22** is stopped, the anode **23** and the cover of the pot are removed, and the depleted bath is decanted off by tilting the pot. Iron powder deposited on the walls of the pot may then be readily removed.

The above described electrolysis procedure and apparatus therefor are the subject of my copending applications Serial No. 214,988, filed March 10, 1951 (now abandoned) and Serial No. 453,898, filed September 2, 1954.

While continuous operation of the electrolytic cell **21** is possible with certain modifications, the advantages to be obtained thereby are not sufficient to justify the complications involved in most instances. By using a plurality of cells and shutting down only one cell at a time for recovery of the iron powder, a fairly uniform supply of dry HCl may be maintained in the conduit **25** leading back to the reactor **14**.

Because of inherent losses of HCl from the condenser **17** in the system as shown, additional HCl must be continuously supplied and, optionally, an amount of chlorine only sufficient to combine with excess hydrogen from the electrolytic cell, at some convenient point. Thus, the Cl_2 and HCl make up tanks **26** and **28** are shown connected to the conduit **25** for use as needed.

The reactor employed in the system of Fig. 1, as shown in the drawing, is externally heated. However, combustible fuel gases may be introduced into the reactor with the HCl and burned therein to supply additional heat as needed. At least in the absence of any substantial amount of added carbon, any carbon resulting from improper combustion of the fuel is insufficient to affect the selectivity of the process.

The presence of free chlorine in the first chloridizing reactor **14** is to be carefully avoided, for Cl_2 readily chloridizes the chromium, even in the absence of carbon, and its presence in any appreciable amount would seriously upset the selectivity of the chloridizing operation and contaminate the sublimate with chromium chloride and ferric chloride. This not only would result in loss of chromium but would also impair the value of the desired ferrous chloride for the production of iron powder.

The system shown in Fig. 1 of the drawing and described above is ideally suited for the treatment of low grade "refractory" type chromite ore, of which there are huge deposits in the U. S. and other countries. The system is particularly suitable for treatment of these ores to remove only a sufficient portion of the iron to produce a treated ore residue having a chromium content and a chromium-iron ratio equivalent or superior to the metallurgical grades of ore which are available only from a

relatively few sources in the world. Thus, the invention makes useful to the metals industry for the first time cheap low grade ores available in huge quantities from local sources at low cost. In addition, the system is well suited to the treatment of other types and grades of ores containing iron and chromium oxides, including metallurgical grades of chromite, to increase the chromium-iron ratio and produce substantially pure iron powder as a by-product.

The combination of the chloridizing reaction to produce a beneficiated chromite ore, as one product, with the electrolysis of the sublimate to produce iron powder, as a second product, and the recovery of HCl from the electrolytic cell for use in chloridizing additional ore, results in a unitary process of particularly great economic significance. The value of the iron powder, under present market conditions, is alone sufficient to substantially cover the cost of operating the entire process, whereby the enhancement of the value of the ore by raising its chromium-iron ratio at least to that of a metallurgical grade of ore may be viewed as having been achieved at very little or no cost. Conversely, the enhanced value of the treated ore residue is sufficient to more than cover the cost of operating the entire process, and the iron powder may be viewed as a valuable by-product obtained without cost.

Referring next to Figure 2, the system shown therein for illustrative purposes is particularly suited for the treatment of chromite ores to produce, as the final products, substantially pure elemental iron powder and substantially pure elemental chromium powder. The system may comprise a hopper or storage bin **30** from which ore to be treated may be drawn as needed; a conduit or suitable conveyor **31** for feeding ore from the hopper **30** to a rotary kiln **32**; a conduit **33** for removing gaseous reaction products from the kiln **32** and transporting them to a condenser **34**; a suitable conduit or conveyor **35** for transporting solid material from the condenser **34** to a temporary storage hopper **36**; a conduit or suitable conveyor **37** for feeding solid material from the storage hopper **36** into a closed electrolytic cell **38**; a hydrogen gas supply conduit **39** for supplying hydrogen gas to the electrolytic cell **38**, preferably through a hollow graphite anode **40** and into the cell adjacent the bottom thereof; a valve-controlled blow-off conduit **41** for diverting gases emerging from the electrolytic cell during a preliminary scavenging operation; a valve-controlled conduit **42** for removing the gases released within the electrolytic cell during electrolysis and conveying them back to the kiln **32**; a source of hydrochloric acid gas **43** connected to the conduit **42** through a branch conduit **44** for supplying additional gas to the system as needed; and, if desired, a source **45** of chlorine connected to the conduit **43** through a branch conduit **46** for supplying sufficient chlorine to react with at least a part of the excess hydrogen normally exhausted from the electrolytic cell **38** (and the electrolytic cell **58** hereinafter mentioned) in admixture with hydrogen chloride. In addition to the foregoing pieces of apparatus, connected together to form a closed circuit similar to that in Fig. 1, the system of Fig. 2 may include a hopper or storage bin **50** for receiving and temporarily storing the substantially iron-free ore residue discharged from the kiln **32**; a conduit or suitable conveyor **51** for feeding the ore residue from the hopper **50** to a second rotary kiln **52**; a conduit **53** for removing gaseous reaction products from the kiln **52** and transporting them to a condenser **54**; a suitable conduit or conveyor **55** for transporting solid material from the condenser **54** to a temporary storage hopper **56**; a conduit or suitable conveyor **57** for feeding solid material from the storage hopper **56** into a closed electrolytic cell **58**; a hydrogen gas supply conduit **59** for supplying hydrogen gas to the electrolytic cell **58**, preferably through a hollow graphite anode **60** and into the cell adjacent the bottom thereof; a conduit **61** for removing gases released within the electrolytic cell **58** and conveying them into the conduit **41** leading from the electrolytic cell **38** back to the first rotary kiln **32**; and any suitable form of receptacle **62** for receiving the substantially iron-free and chromium-free ore residue from the second rotary kiln **52**.

In this system also the rotary kilns **32** and **52** may be of either the internally or externally fired variety, preferably mounted for rotation about a horizontal axis and tiltable to discharge the solid contents thereof at intervals as desired. The detailed construction of the kilns forms no part of the present invention and any form of kiln employed in the art for similar purposes may be used.

The condensers **34** and **54** and the electrolytic cells **38** and **58** may be identical with the condenser **17** and electrolytic cell **21** of Fig. 1. Also, as in the system of Fig. 1, a plurality of electrolytic cells may be employed to maintain continuous operation and insure a fairly constant flow of dry HCl back to the reactor **14**.

When operating the system shown in Fig. 2, finely granulated ore from the ore storage hopper **30**, preferably containing no free carbon, is charged into the first rotary kiln **32** and is heated therein to a temperature in the range from about 900° to about 1400° C. While maintaining the ore in the kiln **32** within this temperature range, and in a state of agitation as a result of rotation of the kiln, the ore is intimately contacted by a stream of dry hydrogen chloride introduced into the kiln from the conduit **42**. To insure complete removal of iron, this kiln is preferably operated on a batch basis. As in the system shown in Fig. 1, the dry hydrogen chloride reacts with ferrous oxide in the ore, converting it to ferrous chloride, which is removed from the kiln in gaseous form as it accumulates therein. In the absence of free carbon, the iron in the original ore may be substantially completely recovered as substantially pure gaseous ferrous chloride, the chromium and other metal oxides remaining in the reactor unaffected by the hydrogen chloride.

After being condensed in the condenser **34** and transported to the electrolytic cell **38** as before, the ferrous chloride is electrolyzed in the electrolytic cell in the presence of hydrogen to produce elemental iron powder in the same manner as in the system shown in Figure 1, the dry HCl gas from the electrolytic cell, along with the excess hydrogen, being routed back through the conduit **42** to the rotary kiln **32**, with or without the addition of a limited amount of chlorine to convert some of the excess hydrogen to HCl.

When the material charged into the rotary kiln **32** has been substantially completely depleted of its original iron oxide content, the ore residue is dumped into the hopper **50**, from which it may be charged as desired into the second rotary kiln **52** for a second roasting operation. An amount of carbon as nearly as possible equal to that which will convert to CO, all of the oxygen of the Cr_2O_3 present in the substantially iron-free ore residue is mixed therewith in the storage hopper **50**, or is charged therewith into the second kiln **52**. Upon bringing the charge of ore residue and carbon to a temperature in the range of about 850° C. to 1100° C. in the second kiln **52**, a stream of straight chlorine gas is introduced into the kiln and brought into intimate contact with the heated and agitated ore and carbon for converting the chromic oxide to gaseous chromic chloride. By limiting the amount of carbon to the quantity that will combine with all of the oxygen of the Cr_2O_3 component of the ore residue being treated, to form carbon monoxide, substantially only the chromium oxide is attacked, and the oxides of calcium, magnesium, aluminum, and silicon again remain substantially unaffected.

The chlorine treatment of the iron-free ore residue in the second kiln **52** is continued until substantially all of the chromium content has been removed as gaseous chromic chloride, at which point the kiln is emptied into the hopper **62** and is ready to receive a second charge from the storage hopper **50**.

If desired, of course, appropriate changes may readily be made in the system shown in Fig. 2 of the drawing whereby the residue from the HCl treatment may be left in the kiln **32**, the necessary carbon added, and chlorine gas introduced to perform the chlorine treatment in the same kiln. While one kiln may thus be eliminated, the separate condenser **54** will generally be required to avoid contamination of one sublimate with the other in the condenser.

The gaseous chromic chloride from the second kiln **52** is condensed in the condenser **54**, transported into the temporary storage hopper **56**, and charged as needed into the second electrolytic cell **58**. Again the electrolysis is carried out by dissolving the material to be electrolyzed in a bath of alkali metal chloride while hydrogen is passed into the cell through the anode **50**, and electrolysis is carried out with a continuous stream of hydrogen being diffused through the bath to react with and remove chlorine gas released at the anode. This electrolysis operation and apparatus therefor are subjects of my above mentioned copending application Serial No. 201,089.

The dry HCl gas recovered from the second electrolytic cell **58** is conducted into the conduit **41** and returned to the first rotary kiln **32** for use in the treatment of additional ore. The chromium metal deposited in the cell is recovered by tilting the cell to decant the exhausted alkali metal chloride bath, whereby the chromium may readily be raked and scraped from the cell for purification in accordance with the process described in my application Serial No. 201,089.

Since the iron content of the original ore is substantially completely removed in the first rotary kiln **32**, the chromic chloride recovered from the second rotary kiln **52** is substantially iron-free. By careful control of the amount of carbon charged into the second kiln **52**, the chromic chloride withdrawn therefrom is also substantially free of contamination with chlorides of any of the other metals commonly present in the original ore. The chromic chloride may readily be produced with a purity at least as high as 99%, and chromium metal of a corresponding purity is obtainable with substantially 100% yield from the second electrolytic cell **58**.

The system of Fig. 2 may also be advantageously employed to produce a carbon free ferro-chromium alloy in the electrolytic cell **58**, instead of pure chromium. In this case, the HCl treatment in the first kiln **32** is terminated before all of the iron has been converted to gaseous ferrous chloride, leaving any desired amount of iron oxide in the ore residue to be charged to the second kiln **52**. When a selected amount of iron oxide is to be left in the ore residue from the HCl treatment, a corresponding amount of carbon may be tolerated in the original charge without danger of contaminating the $FeCl_2$ sublimate with $CrCl_3$. However, no advantage is obtained by having carbon present at this stage in the process, and it is preferable that none be employed.

The ore residue discharged from the kiln **32**, after having its chromium:iron ratio reduced to any desired degree, may be mixed in the container **50** with enough carbon to react with all of the oxygen of both the chromium oxide and iron oxide. Alternatively the required amount of carbon may be added directly to the second kiln **52** with the ore residue from the container **50**. Upon treatment of this mixture with chlorine in the kiln **52** at a temperature between about 850° and 1100° C., all of the chromium and iron may be converted to $CrCl_3$ and $FeCl_3$, sublimed together, and condensed together in the condenser **57**. Again, the sublimate is substantially free from contamination with any of the gangue metals or compounds thereof, and a substantially pure mixture of $CrCl_3$ and $FeCl_3$ is recovered from the condenser **56**.

As disclosed in my above mentioned application Serial No. 453,898, filed September 2, 1954, for Fused Bath Electrolysis of Metal Chlorides, electrolysis of such a mixture of chromium and iron chlorides in a fused alkali metal chloride bath, with excess hydrogen diffused through the bath, results in deposition of a carbon-free ferro-chromium alloy on the cathode of the cell. The proportions of chromium and iron in the deposited alloy substantially correspond to the proportions of the chromium and iron chlorides in the bath, and excellent yields of a high purity alloy are obtained. Thus, when charging the mixed chlorides from the condenser **54** into the second electrolytic cell **58**, and operating it in the same manner as when straight $CrCl_3$ is to be electrolyzed, the final products of the system are iron powder from the first electrolytic cell **38** and ferro-chromium powder from the second electrolytic cell **58**, both products being produced in a state of high purity with recovery in these two commercially valuable forms of substantially all of both the iron and chromium of the original ore.

EXAMPLE 1

A. *High grade Philippine ore*

Temperature ---------- ° C-- 900
Time ---------- hours-- 1

Analysis before treatment:

	Per cent
Cr_2O_3	49.80
FeO	10.22

(Cr:Fe=4.3:1)

Analysis of residue:

	Per cent
Cr_2O_3	65.0
FeO	3.86

(Cr:Fe=14.7:1)

Sublimate: 99% $FeCl_2$, 0.65% $CrCl_3$

B. *Low grade Philippine ore*

Temperature ---------- ° C-- 950
Time ---------- hours-- 2

Analysis before treatment:

	Per cent
Cr_2O_3	32.68
FeO	12.78

(Cr:Fe=2.26:1)

Analysis of residue:

	Per cent
Cr_2O_3	42.34
FeO	3.68

(Cr:Fe=10.1:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

C. *Low grade Philippine ore (same as B)*

Temperature ---------- ° C-- 950
Time ---------- hours-- ¼

Analysis of residue:

	Per cent
Cr_2O_3	40.71
FeO	4.85

(Cr:Fe=7.43:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

D. *South African ore*

Temperature ---------- ° C-- 900
Time ---------- hours-- ¼

Analysis before treatment:

	Per cent
Cr_2O_3	45.02
FeO	20.51

(Cr:Fe—1.89:1)

Analysis of residue:

	Per cent
Cr_2O_3	54.44
FeO	10.98

(Cr:Fe=4.36:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

E. *South African ore (same as D)*

Temperature ---------- ° C-- 900
Time ---------- hours-- 2

Analysis of residue:

	Per cent
Cr_2O_3	65.30
FeO	1.70

(Cr:Fe=33.8:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

F. *Rhodesia ore*

Temperature ---------- ° C-- 950
Time ---------- hours-- ¼

Analysis before treatment:

	Per cent
Cr_2O_3	44.00
FeO	9.09

(Cr:Fe=4.25:1)

Analysis of residue:

	Per cent
Cr_2O_3	45.35
FeO	7.61

(Cr:Fe=5.23:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

G. *Rhodesia ore (same as F)*

Temperature ---------- ° C-- 950
Time ---------- hours-- 2

Analysis of residue:

	Per cent
Cr_2O_3	51.10
FeO	1.56

(Cr:Fe=28.8:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

H. *Montana ore (Mouat)*

Temperature ---------- ° C-- 950
Time ---------- hours-- 1

Analysis before treatment:

	Per cent
Cr_2O_3	37.20
FeO	12.49

(Cr:Fe=2.62:1)

Analysis of residue:

	Per cent
Cr_2O_3	39.56
FeO	9.93

(Cr:Fe=3.50:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

I. *Montana ore (same as H)*

Temperature ---------- °C.-- 950–1050
Time ---------- hours-- 3

Analysis of residue:

	Per cent
Cr_2O_3	46.20
FeO	6.57

(Cr:Fe=6.18:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

J. *Montana ore (Mouat—different sample)*

Temperature ---------- °C.-- 950
Time ---------- hours-- 4

Analysis before treatment:

	Per cent
Cr_2O_3	39.20
FeO	14.76

(Cr:Fe=2.32:1)

Analysis of residue:

	Per cent
Cr_2O_3	49.98
FeO	4.19

(Cr:Fe=10.5:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

K. *Montana ore (Benbow)*

Temperature ---------- °C.-- 950
Time ---------- hours-- 5

Analysis before treatment:

	Per cent
Cr_2O_3	44.60
FeO	21.41

(Cr:Fe=1.83:1)

Analysis of residue:

	Per cent
Cr_2O_3	56.07
FeO	0.77

(Cr:Fe=64.0:1)

Sublimate: 99+% $FeCl_2$, trace of $CrCl_3$

L. *Montana ore (same as K)*

Temperature ---------- °C.-- 1000
Time ---------- hours-- 5

Analysis of residue:

	Per cent
Cr_2O_3	56.30
FeO	0.65

(Cr:Fe=75.0:1)

Sublimate: 99+% $FeCl_2$, trace $CrCl_3$

From the foregoing tests of representative ores of different grades, it is apparent that the chromium:iron ratio may be raised at will until substantially all the iron is eliminated while recovering a sublimate of better than 99% $FeCl_2$. From a comparison of the last two tests K and L, it will also be observed that substantially optimum results may be obtained at about 950° to 1000° C.

EXAMPLE 2

To illustrate the effectiveness of the Cl_2 treatment of a substantially iron-free residue to produce $CrCl_3$, the residue from Test L of Example 1 was mixed with just enough carbon to react with the oxygen of the Cr_2O_3 and form CO. The mixture was then heated in straight Cl_2 at a temperature of about 950° C. for 2 hours. The sublimate from this treatment was collected, condensed, and analyzed with the following results:

	Per cent
$CrCl_3$	99+
$FeCl_2$ and/or $FeCl_3$	0.40

The residue after this chlorine treatment contained only traces of iron and chromium, and the sublimate contained only traces of any of the other gangue metals. If excess carbon had been used, however, substantially all of the aluminum and silicon and some magnesium and calcium would also have been chloridized and sublimed with the chromium, necessitating carefully controlled fractional condensation, which is economically impractical, as pointed out above.

EXAMPLE 3

Another treatment of the high grade Philippine ore of Example 1A with dry HCl yielded a residue analyzing 60.40% Cr_2O_3 and 2.75% FeO. When this residue was treated first with chlorine gas in the absence of carbon, there was an impractically slow reaction at temperatures up to as high as 1050° C. However, when the residue was mixed with just the amount of carbon which would react with the oxygen of the Cr_2O_3 to produce CO, and the mixture was treated at 1000° C., the removal of chromium and iron was substantially complete in less than 1 hour. Analysis of the sublimate showed no

chlorides of gangue metals, the sublimate being a mixture consisting of 97.8% Cr_2Cl_3 and the balance $FeCl_3$.

Example 3 illustrates, first, that the action of chlorine gas on a residue containing a large amount of Cr_2O_3 and only a very small amount of FeO is impractically slow unless carbon is added to take care of the oxygen of the chromium and iron oxides.

EXAMPLE 4

A Montana Mouat ore analyzing 37.20% Cr_2O_3 and 12.4% FeO (Cr:Fe=2.60:1) was first treated with HCl for one hour at 900° C. to produce ferrous chloride and a residue designated residue A. A second sample of the same ore was treated for three hours with HCl at 950° C. to produce ferrous chloride and a residue designated residue B. The residues A and B analyzed as follows:

Residue A	Residue B
9.50% FeO 39.56% Cr_2O_3 (Cr:Fe=3.9:1)	6.57% FeO 46.20% Cr_2O_3 (Cr:Fe=6.2:1)

Residues A and B were then mixed with just sufficient carbon to convert all of the oxygen of the chromium and iron oxides to carbon monoxide, and the mixtures were treated with chlorine gas at 950° C. for one hour. The sublimates from these two treatments, respectively designated sublimates A and B, analyzed as follows:

Sublimate A	Sublimate B
19.50% $FeCl_3$ Balance $CrCl_3$ (Cr:Fe=4.09:1)	11.34 $FeCl_3$ Balance $CrCl_3$ (Cr:Fe=7.70:1)

The foregoing examples 2, 3 and 4 illustrate the practicality of producing either substantially pure $CrCl_3$ or substantially pure mixtures of $CrCl_3$ and $FeCl_3$, depending upon the amount of iron oxide in the residue treated, by gassing the residue with Cl_2 in the presence of the theoretically required amount of carbon. The carbon apparently reacts preferentially with the chromium and iron oxides and leaves the gangue materials substantially unaffected in the final residue. At most, only mere traces of the gangue metals, aluminum, silicon, magnesium, and calcium, are detectable in the sublimate, and the proportion of iron in the sublimate is substantially the same as in the residue treated with chromium.

The two chloridizing reactions are sufficiently selective, when controlled as described, so that iron and chromium powders, or iron and ferro-chromium powders, of better than 99% purity can be produced by electrolysis of the two sublimates.

The particular chloridizing agents and the chlorodizing conditions employed in accordance with the invention are highly critical in obtaining commercially useful results. For example, during the HCl treatment of a chromite ore, the presence of more carbon than the limiting quantity mentioned above causes the HCl to chloridize chromium as well as iron, though more slowly. Within the preferred temperature range (900° to 1050° C.), given sufficient carbon with the ore, iron chloride begins to come off first, then a mixture of iron and chromium chlorides comes off, and gradually the sublimate becomes richer in chromium chloride and leaner in iron chloride until the former is present in a great preponderance over the iron. While the sublimation temperature of iron chloride is somewhat below that of chromium chloride, vaporization of the former at a practical rate is not feasible below the sublimation point of the latter. Also, depending upon various factors, the temperature of formation of the chlorides is often above their sublimation temperatures. Accordingly, when chlorides of both iron and chromium are formed together, selective sublimation of the iron chloride alone at a practical rate is substantially impossible.

Since the HCl treatment for removal of iron chlorides does not require the presence of any carbon, there is no reason for purposely adding any carbon to the first reactor or kiln **14** (Figure 1) or **32** (Figure 2). It is interesting to note, however, that the limited amount of carbon specified above may be tolerated during the HCl treatment. Why such an amount of carbon, which is apparently not actually used by the iron oxide, has no effect, whereas a larger amount causes the chromium to react and produce $CrCl_3$ is not at all clear. As a result, the tolerable amount of carbon is dependent upon presently unknown factors, and it may be sheer coincidence that such limit can be related to the amount of oxygen in the iron oxide to be left in the first ore residue.

The fact that the presence of some carbon may be tolerated permits greater freedom in the selection and use of fuels to be burned in contact with the ore where internal heating of the kiln is desired. Substantially complete freedom from carbon during the HCl treatment is preferred and is the best guarantee that the maximum tolerable amount will not be exceeded.

If chlorine gas is substituted in whole or even in a small part for the dry HCl gas in the initial chloridization of an ore containing a substantial amount of FeO, even in the presence of limited amounts of carbon or no carbon at all, the selective formation and/or volatilization of iron chloride alone is apparently not feasible at a commercially practical rate, for the chlorine attacks both the chrominum and the iron with the production of chromium chloride in the sublimate. While the presence of a substantial amount of carbon is necessary to effect the rapid chloridization of Cr_2O_3 with chlorine when little or no FeO is present, the presence of a substantial amount of FeO seems to render the Cr_2O_3 more susceptible to attack by chlorine in the absence of carbon, and a chloridizing agent containing appreciable free chlorine is wholly unsuited for selectively chloridizing only the iron component of an ore. Moreover, chlorine converts FeO to $FeCl_3$, rather than $FeCl_2$, which is less suited for electrolysis because of the greater amount of power required for its reduction.

Phosgene and carbon tetrachloride, both being more active than chlorine, are even more objectionable than chlorine as a possible substitute for dry HCl for they attack the other oxides of the ore as well as the chromium and iron oxides, and do so at relatively much lower temperatures. As a result, the sublimate is contaminated with chlorides of aluminum and silicon, and, sometimes, also with the chlorides of magnesium and calcium.

The presence of any appreciable amount of water vapor during the HCl treatment seriously retards the chloridization of the iron oxide and renders the process commercially impractical, if not totally inoperative. Thus, completely dry HCl gas is preferred for the first chloridization treatment, and only very minor amounts of water vapor can be tolerated in commercial operations.

Attempts to use vapors from concentrated hydrochloric acid in the HCl treatment have resulted not only in extremely slow reaction, but have also resulted in the absorption of so much water by the small amounts of iron chloride formed that the iron chloride is saturated and may even become an aqueous solution.

In various prior art patents, reference is made to the introduction of substantial amounts of oxygen with the chloridizing reagents employed. While this may perform some useful function where lower temperatures and appropriate chloridizing reagents are employed to form chlorides without volatilizing them, it is to be carefully avoided at temperatures of 850° C. or higher. At such temperatures the presence of oxygen in any material amount converts both chromium and iron chlorides to oxy-chlorides and may even carry the metals back to the

oxide stage, thus working directly at cross-purposes with the primary objects of the invention.

While dry HCl gas, in the presence of sufficient carbon, will attack the chromium oxide as noted above, this chloridizing reagent is impractical for use in treating the iron-free residue in the second chloridizing reacton because it is not sufficiently active, and excessive times and temperatures are required, as shown in Example 3. The use of phosgene or sulphur tetrachloride in the second chloridizing reaction, on the other hand, is impractical because these reagents attack the other oxides of the residue and result in contamination of the chromium chloride with chlorides of aluminum and silicon and, in some cases, with the chlorides of magnesium and calcium as well. Thus, chlorine gas is by far the most satisfactory chloridizing agent yet found for treatment of the iron-free residue to produce pure chromium chloride.

From the foregoing, it will be appreciated that I have provided a method and system by which all of the various objects of the invention may be accomplished. By means of the invention, low grade chromite ores are, for the first time, rendered practically and economically suitable for numerous uses that formerly required metallurgical grades of ores or were not feasible by any known process. In addition, an economical process has been provided for producing from the low grade ores, as well as from the high grade ores, substantially pure iron, chromium, and ferro-chromium in powdered form.

Having described my invention, I claim:

1. A process for beneficiating chromite to increase the chromium-to-iron ratio by selectively forming and subliming ferrous chloride, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed; free chlorine and active oxidizing gases and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue.

2. The process of claim 1 in which said elevated temperature is between about 900° and 1050° C.

3. A process for producing anhydrous ferrous chloride from chromite by treating the chromite to selectively form and sublime ferrous chloride, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed and condensing it under anhydrous conditions; free chlorine and active oxidizing gases and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue.

4. The process of claim 3 in which said elevated temperature is between about 900° and 1050° C.

5. The process of claim 3 in which said gaseous ferrous chloride removed from said chamber is condensed at a temperature between about 350° and 650° C. while removing, in vapor form, any water entrained with the gaseous ferrous chloride.

6. A process for producing ferrous chloride from ore containing oxides of iron and chromium by treating the ore to selectively form and sublime ferrous chloride, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue.

7. The process of claim 6 in which the gaseous ferrous chloride removed from said chamber is condensed to an anhydrous powder at a temperature between about 350° and 650° C. while removing, in vapor form, any water entrained with the gaseous ferrous chloride.

8. A process for producing ferrous chloride from ore containing oxides of iron and chromium by treating the ore to selectively form and sublime ferrous chloride, comprising continuously feeding said ore preheated above about 1000° C. into a reaction chamber, continuously contacting the ore in said chamber under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride while maintaining the temperature of the ore above about 850° C., continuously removing from said chamber gaseous ferrous chloride as it is formed, and continuously removing an iron-impoverished ore residue from said chamber; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue as it is discharged from said chamber, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue.

9. The process of claim 8 in which the gaseous ferrous chloride removed from said chamber is condensed to an anhydrous powder at a temperature between about 350° and 650° C. while removing, in vapor form, any water entrained with the gaseous ferrous chloride.

10. A process for recovering iron and chromium values from ore containing oxides of iron and chromium, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed and condensing it under anhydrous conditions; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue; contacting the ore residue with chlorine gas at a temperature above about 850° C. in the presence of carbon in an amount sufficient to react with the oxygen of the remaining iron and chromium oxides, to convert the chromium and remaining iron, if any, to gaseous chromic and ferric chlorides, and removing the resulting gaseous chromic chloride and any gaseous ferric chloride as they are formed and condensing them under anhydrous conditions.

11. The process of claim 10 in which said elevated temperatures are between about 900° and 1050° C.

12. A process for producing iron powder from chromium-iron ores and leaving a beneficiated, high-chromium, iron-impoverished ore residue, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the

ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue; condensing the removed gaseous ferrous chloride at a temperature above about 350° C. while separating entrained water vapor formed therewith to produce anhydrous ferrous chloride in powder form, electrolytically disassociating the anhydrous ferrous chloride in a fused bath consisting essentially of alkali metal chloride in an electrolytic cell while diffusing hydrogen gas through the bath, to deposit elemental iron on the cathode of the cell and produce dry hydrogen chloride; and returning the dry hydrogen chloride to said chamber for contacting additional ore.

13. The process of claim 12 in which the temperature in said chamber is between about 900° and 1050° C.

14. A process for producing iron powder from chromium-iron ores and recovering a beneficiated, high-chromium, iron-impoverished ore residue, comprising contacting the ore in a chamber at a temperature between about 850° and 1100° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue with a reduced amount of iron; condensing the removed gaseous ferrous chloride at a temperature sufficiently above the boiling point of water, while separating entrained water in vapor form, to produce anhydrous ferrous chloride in powder form, melting the anhydrous ferrous chloride in a fused bath consisting essentially of alkali metal chloride in an electrolytic cell, electrolyzing the ferrous chloride in said bath while diffusing hydrogen gas therethrough to deposit elemental iron powder on the cathode and release chlorine at the anode for reaction with the diffused hydrogen, and withdrawing dry hydrogen chloride so formed and returning it to said chamber for contacting additional ore; recovering a high-chromium, iron-impoverished ore residue from said chamber; and recovering elemental iron powder from said electrolytic cell.

15. The process of claim 14 in which the temperature in said chamber is between about 900° and 1050° C., and the gaseous ferrous chloride removed from said chamber is condensed at a temperature between about 350° and 650° C.

16. The process of claim 14 in which ore preheated to above about 1000° C. is continuously fed into said chamber, said gaseous reagent is continuously fed into said chamber counter-current to the feed of the ore, and said high-chromium, iron-impoverished ore residue is continuously removed from said chamber.

17. The process of claim 14 in which ore preheated to above about 1000° C., is continuously fed into said chamber, said gaseous reagent is continuously fed into said chamber counter-current to the feed of the ore, said high-chromium, iron-impoverished ore residue is continuously removed from said chamber, and gaseous ferrous chloride is continuously removed from said chamber together with entrained water vapor formed therewith and passed into a condenser maintained at a temperature between about 350° and 650° C., said water vapor being continuously withdrawn uncondensed from said condenser, and the ferrous chloride being deposited in the condenser as a substantially anhyrous powder.

18. A process for recovering iron and chromium from chromium-iron ores, comprising contacting the ore in a chamber at a temperature above about 850° C. under anhydrous conditions with a gaseous reagent consisting essentially of dry hydrogen chloride, and removing gaseous ferrous chloride from said chamber as it is formed and condensing it under anhydrous conditions; free chlorine, active oxidizing gases, and active reducing gases being excluded from said chamber during the reaction, and any free carbon in the chamber during the reaction being limited to an amount not exceeding one part to six parts by weight of any iron oxide left in the ore residue at the end of the reaction, whereby substantially the entire chromium content of the ore remains as oxide in the ore residue; electrolyzing the condensed ferrous chloride in a fused bath of alkali metal chloride in a first electrolytic cell while diffusing hydrogen through the bath to deposit iron powder on the cathode and release chlorine for reaction with said hydrogen to produce dry hydrogen chloride; contacting said ore residue with chlorine gas at a temperature above about 850° C. in the presence of carbon in an amount sufficient to react with the oxygen of the remaining iron and chromium oxides, to convert the chromium and remaining iron, if any, to gaseous chromic and ferric chlorides, and removing the resulting gaseous chromic chloride and any gaseous ferric chloride as they are formed and condensing them under anhydrous conditions; electrolyzing the condensed chromic chloride and any ferric chloride condensed therewith in a fused bath consisting essentially of alkali metal chloride in a second electrolytic cell while diffusing hydrogen therethrough to deposit the chromium and any iron present as a powder on the cathode and release chlorine for reaction with said hydrogen to produce dry hydrogen chloride; removing dry hydrogen chloride from said cells and feeding it into said chamber for contacting additional ore; and recovering elemental iron powder from said first electrolytic cell; and recovering elemental chromium, alloyed with any iron present, from said second electrolytic cell.

19. The process of claim 18 in which the contacting of said ore with dry hydrogen chloride and the contacting of said ore residue with chlorine are both carried out between about 850° and 1100° C.

20. The process of claim 18 in which the gaseous ferrous chloride, and the gaseous chromic chloride together with any ferric chloride formed therewith, are condensed at a temperature between about 350° and 650° C. while removing in vapor form any water entrained therewith.

21. The process of claim 18 in which the contacting of said ore with dry hydrogen chloride and the contacting of said ore residue with chlorine are both carried out between about 850° and 1100° C., the contacting of the ore with dry hydrogen chloride and the removal of ferrous chloride being continued until a substantially iron-free residue remains, whereby the metal powder recovered from said second electrolytic cell is substantially pure chromium.

22. The process of claim 18 in which ore preheated to above about 1000° C. is continuously fed into said chamber, said gaseous reagent is continuously fed into said chamber counter-current to the feed of said ore, said ore residue is continuously withdrawn from said chamber and continuously fed into a second chamber for reaction with chlorine, the chromic chloride and any ferric chloride formed therewith are continuously removed from said second chamber, a substantially iron-free and chromium-free ore residue is continuously withdrawn from said second chamber, and dry hydrogen chloride from at least one of said electrolytic cells is continuously fed to the first mentioned chamber for contacting additional ore.

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