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TREATMENT OF CHROMIUM ORES

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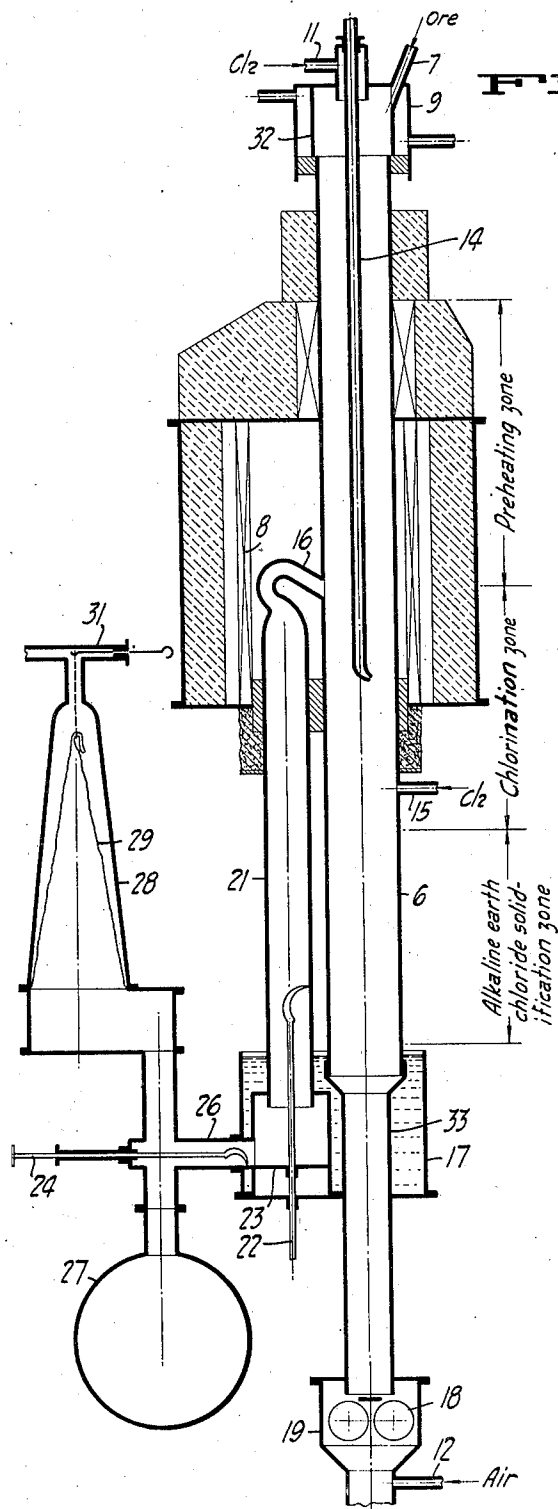
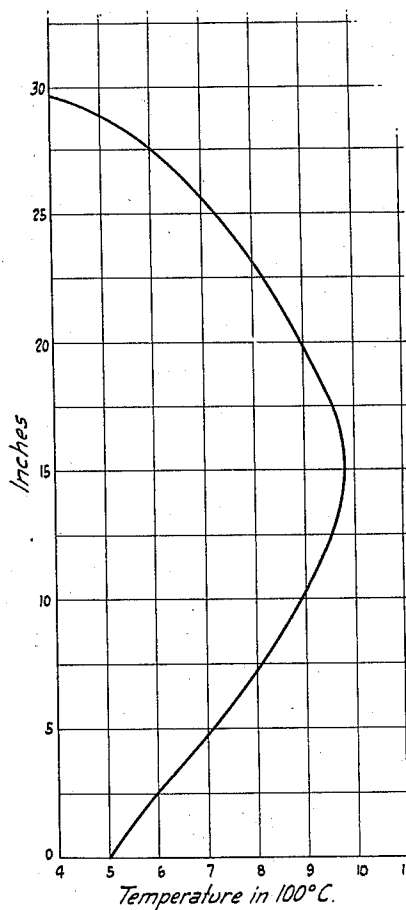


FIG. 1

FIG. 2



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TREATMENT OF CHROMIUM ORES

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16 Claims. (Cl. 75—112)

This application is a continuation in part of application Serial Number 372,412 filed December 30, 1940.

This invention relates particularly to improved methods of chlorination of oxidic ores carried out at elevated temperatures in which carbonaceous materials are used with chlorine to accomplish the chlorination. It is especially adapted to chlorination of chromite ore; the methods disclosed are of advantage in the treatment of all ores containing alkaline earths such as magnesium in such an amount as to present a sintering problem upon chlorination of the ore.

In practice, chromite ore is introduced into a suitable furnace, usually a vertical column, along with a carbonaceous reducing agent. Chlorine is usually introduced into the furnace to pass counter-current to the ore. Temperatures suitable for the reduction and chlorination are maintained in the furnace, the maximum usually being between 950° C. and 1050° C. although temperatures as high as 1250° C. can be employed. In use, certain portions of the furnace are devoted to definite operations; and in the direction of ore passage through the furnace I have for convenience designated these as the "preheating zone" wherein the ore is preheated, and the "chlorination zone" wherein the actual reduction and chlorination occurs. Chlorine is usually introduced just below or beyond the actual chlorination zone, usually at a point in the column which, in the direction of ore passage, is beyond the point of maximum temperature; in the case of chromite ore usually in a region at a temperature of about 850° to 950° C.

In the continuous reduction and chlorination of a chromite ore according to the method outlined, that is with carbon and chlorine in a vertical column arranged for gravitational passage of ore, continuous operation was occasionally hampered by formation of a solid, ringlike flow restricting accretion on the side wall of the column below the "chlorination zone." These were found to be made up of ore and carbon bonded together largely by magnesium chloride. Such a ring was removed from the furnace only with difficulty; frequently it could be removed only by shutting down, cleaning out the column and breaking up the ring. Ring or accretion formation was more frequent and more aggravating when the rate of throughput of the ore was high. One of the limiting factors on the rate of throughput was the formation of these undesirable solidified masses on the wall defining the ore column. Apparently these accretions or

rings are due to materials in the ore, such as lime and magnesia, that are converted by chlorination into the corresponding chlorides which are fusible at the temperature of the chlorination.

These molten chlorides upon solidifying may bond the ore particles together into a mass capable of forming a bridge within the column or accretions upon the wall of the column. Such a mass is cemented or agglomerated by solidification of the molten chlorides. The problem is particularly prevalent when low grade chromite ores high in magnesia are employed; domestic ores are usually of this character.

I have found that if, in that region in the furnace below the "chlorination zone," which I will, for convenience, term the "alkaline earth chloride solidification zone" or "solidification zone," I maintain an atmosphere which is free of chlorine and hydrogen chloride and is not adsorbed to any appreciable extent by the molten alkaline earth chlorides, these difficulties are overcome. The "solidification zone" extends from a point in the column, in the direction of ore passage, which is at a temperature just below or at the melting point of magnesium chloride and calcium chloride and through the solidification range of these chlorides and any other like molten chlorides present. I have observed that the chlorides of calcium and magnesium do not wet silica in the presence of chlorine or hydrogen chloride, but do wet more easily in an atmosphere of nitrogen, carbon monoxide, helium, argon, or other gas non-adsorbable by the molten chlorides, which atmosphere is free from chloride and hydrogen chloride. Thus the absence of chlorine and hydrogen chloride in the column through the critical solidification temperature range of the alkaline earth chlorides results in the formation of a uniform film of magnesium chloride and calcium chloride on the carrier particles or siliceous ore residue present. In the presence of hydrogen chloride or chlorine, however, globules of magnesium chloride tend to form which coalesce and descend as a liquid stream. When these streams solidify they bond together whatever they are in contact with at the moment.

The "solidification zone," and its chlorine, and hydrogen chloride free, non-adsorbable gas atmosphere, are therefore maintained in the column immediately below the "chlorination zone" and in that region wherein the molten alkaline earth chlorides solidify. Under this condition, the magnesium chloride, calcium chloride and other like chlorides, uniformly wet the remain-

ing silicious material present (silica not being reduced or chlorinated under the furnace conditions) and are carried out on this instead of collecting and falling as liquid masses to solidify on the walls of the furnace or on masses of residue material in the cooler regions of the furnace.

To ensure that the "solidification zone" is maintained in its proper relation to the "chlorination zone," the point of introduction of the chlorine into the "chlorination zone" and the region wherein the non-adsorbable gas atmosphere is maintained must be established in a proper spaced relationship. That point in the furnace which is at the temperature of fusion of the principal alkaline earth chloride provides a generally critical upper limit in the furnace for the "solidification zone." The non-adsorbable gas must be introduced into the furnace beyond or below that region which is at this temperature if it is to be effective in enabling the chlorides to wet uniformly the silicious material. When magnesium chloride is the chief chloride to which attention must be given, its fusion temperature, 708°-711° C. is a critical upper limit for location of the non-adsorbable gas inlet. It is generally immaterial how far below the fusion temperature point in the furnace the non-adsorbable gas is introduced, the essential factor being a spatial separation of the gas and chlorine inlets below and above the critical point to ensure existence of definite and effective "solidification" and "chlorination" zones. Introduction of the non-adsorbable gas and its function will be further discussed.

The preferred process of this invention is one wherein a considerable portion of the chlorine, if not all, is passed counter current to the ore stream. Consequently at least some of the chlorine is introduced at a point in the "chlorination zone" below the point of maximum temperature. For reasons which will be presently explained, the inlet for this chlorine must be provided at a point sufficiently spaced from the "solidification zone." If the chlorine inlet is too close to the "solidification zone," the "chlorination zone" will extend too far in the direction of ore passage, possibly even into a region which is at a temperature where chromic chloride will condense in the ore stream. Additionally, the length of the non-adsorbable gas treating column will be undesirably reduced. If the chlorine inlet is too close to the point of maximum temperature in the "chlorination zone," the length of this will be shortened by the cooling action of the chlorine fed at ordinary temperatures while the length of time that the ore is subjected to chlorine will be unduly decreased.

I have found that the best point for introduction of chlorine in the "chlorination zone" is about half way between (a) the off-take from the furnace for sublimed chlorides and (b) the point at which the temperature in the furnace corresponds to the fusion temperature of the principal alkaline earth chloride present. In the case of chromite ores wherein magnesium chloride is the principal molten chloride formed, this is usually at a point which is at or about 900° C.; provided, however, that the point of entrance of chlorine when using the present invention with the auxiliary gas, should not be below the normal condensation point of the vapors of chromium trichloride. This is near 850° C. for most chromite ores.

Chlorine is introduced in an amount sufficiently great to satisfy the stoichiometric require-

ments of the ore plus an excess adequate to maintain about 10% free chlorine in the exit gases from the retort after condensation of sublimed chlorides for reasons pointed out at length in my Patent 2,133,998 of October 25, 1938. At times not all of the chlorine need be added counter-currently below the "chlorination zone." The total requirements may be met by supplying from 50% to 75% of the chlorine counter-currently below the vapor exit, and the remainder concurrently from above. This serves to increase the proportion of carbonyl or carbon chlorides which may be formed in the "chlorination zone" between the lower chlorine inlet and the vapor exit, as will be presently explained; it further increases the effective length of the "chlorination zone," as well as helping to sweep volatile chlorides from the ore column above the "chlorination zone."

The chlorine and hydrogen chloride free, non-adsorbable gas atmosphere to be maintained in the "solidification zone" can be provided by introducing carbon monoxide, nitrogen, helium, argon or other suitable gas at the proper point in the furnace. Instead of introducing carbon monoxide as such it is possible to introduce oxygen, or an oxygen source as air, or a material decomposable in the column to yield oxygen, as a peroxide, a nitrate, chlorate or per-oxy compound, to react with carbon present in the hot residue in the furnace beyond the chlorination zone to form carbon monoxide. When decomposable materials are added, they are introduced at a point in the "solidification zone" whereas sufficient heat is present to ensure oxygen release and reaction to form carbon monoxide.

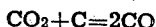
The use of air is probably the simplest manner of practicing the invention when excess carbon is present. Further, the use of carbon monoxide has certain unique advantages which will now be pointed out. It has been recognized by those experienced in the chlorination of ores using carbonaceous materials with chlorine that considerable stoichiometric carbon excesses (usually 20%-30%) are required in order to secure high extraction of the metal values in the ores treated. Some carbon must therefore still be present when the last of the metal oxide particles in the ore are being chlorinated. In a continuous counter-current unit, this corresponds to the point of exit of the ore residue from the chlorination zone. Further, it has long been recognized that chlorinated carbonaceous compounds, such as the chlorides of carbon, or carbon compounds incompletely saturated with oxygen such as carbon monoxide or carbonyl chloride, produced an exceptionally smooth and readily controllable chlorination. The value or cost of such materials is usually prohibitive for commercial chlorination of ores. By using air to form carbon monoxide, the advantages of using carbon chlorides can be secured without their high cost when they are produced and used as such.

The manner in which the process of my invention operates with oxygen and excess carbon may be clarified by the following discussion: Oxygen, supplied in any convenient manner as by introducing air below the "solidification zone," contacts excess carbon in the spent ore in the "solidification zone" and reacts, at least in part, in the absence of chlorine, to form carbon monoxide. The carbon excess required is determined by the requirements empirically found for the reduction and chlorination of the ore in the "chlorination zone." Usually this excess is about

25% more than the stoichiometric requirements for all reductions and chlorinations occurring and producing carbon dioxide and chlorides. The quantity of oxygen made available in the "solidification zone" for reaction with the carbon excess is sufficient stoichiometrically to react to form carbon monoxide with only a substantial portion, from 50% to 85%, of the carbon present in excess of that required by the stoichiometry of the reduction-chlorination reactions.

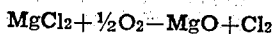
When the carbon monoxide produced in that part of the column below the chlorine inlet comes into contact with chlorine in the "chlorination zone," carbonyl chloride and chlorides of carbon are formed, which at these temperatures react rapidly with the ore in a chlorination reaction. The carbon monoxide of the "solidification zone" gas stream is thus completely utilized.

It might be assumed that the introduction of some air or oxygen with the chlorine fed directly to the "chlorination zone" would first cause the formation of carbon monoxide, by interaction of carbon and oxygen, and the carbon monoxide so formed could then react partly with chlorine to form carbonyl chloride, which in turn would act as a chlorinating agent, and thus permit the first chlorination. Such action is, however, very minor. Since it is desired to operate at temperatures whereat the chlorination of the ore is rapid, and with an excess of chlorine, the product of the chlorination reaction is always carbon dioxide rather than carbon monoxide. Furthermore, it is well known that the first step of the oxidation of carbon itself is invariably carbon dioxide rather than carbon monoxide and that the latter material is obtainable as a secondary formation according to the so-called "producer gas" reaction:



Repeated analyses have shown no carbon monoxide but only carbon dioxide in a normally operated chlorination reaction whence it is clear that no substantial amount of carbonyl chloride can be formed when oxygen and chlorine are simultaneously present as such in the chlorination zone. The conditions for chlorination are thus opposed to the conditions desired for formation of carbonyl chloride, and cannot be effectively produced simultaneously. This emphasizes the necessity for the correct spacial separation of the chlorine inlet and the non-adsorbable gas inlet so that the proper and separate "chlorination zone" and "solidification zone" are maintained.

It might be further thought that the admission of air or oxygen containing gases could promote the reaction



and thus maintain the magnesia in the form of oxide. This has not been found to be the case in practice. Obviously the conditions suited to this reaction are generally ill suited to the chlorination of ore. The conclusion is, therefore, that when oxygen and chlorine together are simultaneously present as such in the chlorination zone, magnesium cannot be prevented from chlorinating nor can it be reoxidized from the chloride form to the oxide form when active chlorination of ore occurs.

Apparatus

As a specific and illustrative example of the manner in which my invention can be carried out successfully, the following operations are disclosed, particularly in conjunction with the ap-

paratus shown in the accompanying drawing in which Figure 1 is a diagrammatic view, partly in section, illustrating an apparatus which I have successfully employed. Figure 2 is a graph illustrating the retort height relative to the temperature maintained.

In this apparatus, a vertical shaft 6 is provided. The shaft is made of inert material as silica, and I have successfully used the material known as Vitreosil. At the upper end of the shaft an ore inlet 7 provides for introduction of the ore charge into casing 32 and thence into the shaft furnace proper.

Heating means, indicated at 8, provided in the form of electrical resistances, is positioned about a portion of the shaft intermediate the ends thereof to provide the "preheating zone" and the "chlorination zone." The upper portion of the shaft 6 is continued by a casing 32 to guide the ore charge into the column. The joint between the shaft and extension is protected by a surrounding water cooling jacket 9. Some chlorine is introduced through an inlet 11 placed at the top of the shaft and the remainder through a side inlet 15 provided toward the end of the "chlorination zone." A movable thermocouple well 14 extends downwardly into the shaft to enable temperatures to be ascertained in the shaft. Exit 16 for volatilized materials is placed above the lower end of the heating zone. At the base of the shaft another cooling section 17 is provided, to protect the joint between shaft 6 and a metal base structure 33 and cool the materials which pass therethrough to be removed by discharge conveyors 18 in case 19 at the bottom of the shaft.

Volatilized products pass over through exit 16 into condenser 21 which is also made of silica, usually Vitreosil. Volatilized chlorides condensing on the side of the condenser 21 are removed by scraper 22 onto plate 23. Another scraper 24 serves to remove condensed chlorides along plate 23 through passage 26, into a receiver 27. Dust, fines and the like are collected by filter bag 29 in housing 28. Rod 31 enables the bag 29 to be shaken to remove collected materials.

Operation

The shaft furnace was brought up to temperature and filled with a charge made up by coating massive carrier particles with a chromite ore-carbon mix. The ore used was of the following composition:

	Per cent
Cr ₂ O ₃	48.1
FeO (total iron).....	19.7
SiO ₂	5.3
MgO.....	16.5
CaO.....	3.8
Mn.....	trace
Al ₂ O ₃ (by difference).....	6.6
	100.0

The chromite ore was first ground to 200 mesh in admixture with 20% free gas carbon. This mixture was then placed on carrier particles prepared and coated after the manner disclosed in my Patent 2,133,997.

The carbon quantity employed was 1.25 times the quantity required stoichiometrically to reduce all reducible oxides present. Air, introduced through the inlet 12 into the column at a point below the "solidification zone" region, reacted with excess carbon present in this region to form carbon monoxide. This was effective as a non-

adsorbable gas atmosphere in the "solidification zone" during the entire run.

The following results are taken from actual operating records showing average conditions maintained during the sixth and the seventh day of continuous operation. They serve to illustrate how continuous operation was maintained in practice with the described apparatus. The charging rate was 4 kilograms per hour of the coated carrier particles. The operation was very smooth and a high chromium conversion was effected.

Days of operation-----	6th	7th
Temperature of vapor exit 16 in ° C-----	1,010	1,045
Ore rate, gms./hr-----	264	308
Chlorine input concurrent from top, liters/hr. (inlet 11)-----	82	89
Chlorine input counter-current from below, liters/hr. (inlet 15)-----	101	109
Air input, liters/hr. (inlet 12)-----	43	46
Ore burden, gms./kg. carrier-----	66	77
Extraction per cent of contained Cr ₂ O ₃ -----	99.4	98.8
Per cent of total MgO retained as oxide-----	2.3	2.2
Per cent of total Mg discharged as magnesium chloride on carrier-----	48.7	74.3
Per cent of total Mg discharged as magnesium chloride in purge-----	1.5	3.1
Per cent of total Mg volatilized as chloride-----	47.5	20.4

It will also be observed that in the two runs, the percentage of oxygen introduced, based on the total chlorine input, was 4.95% for the sixth day's run and 4.84% for the seventh.

Operation temperatures

The temperatures in the retort vary over a considerable range and in Figure 2 I have indicated a typical thermal gradient through the retort. The highest temperature in the retort which is of significance, so far as the sublimed ingredients condensing in condenser 21 are concerned, is that immediately adjacent the vapor off-take 16 for this determines the composition of the mixed chlorides condensing. In case it is desired to have a large percentage of magnesium chloride and other accretion forming chlorides in the condensed mass, the temperature can be maintained relatively high for magnesium chloride and the other chlorides are then more volatile. Temperatures of 1150° C. and upwards to 1400° C. can be used. I prefer, however, to maintain the condensate or sublimate in the receiver as free of magnesium chloride as is possible and therefore operate at a temperature of about 900° C. and usually between 900° C. and 1100° C.

The purging operation

In the above tabulation of operations mention is made of "Mg discharged as magnesium chloride in purge." This following is in explanation of this:

When the retort material is of silica the dispersing action of the inert, chlorine free gas causes the walls of the retort to also be wet in a manner similar to the silicious carrier particles or ore residue. After extended operating periods, this may cause the slow formation of a ring near the upper end of the "Solidification zone," although much less soon than if no non-adsorbable gas atmosphere is employed. This small quantity of magnesium chloride dispersed on the

walls is advantageously removed by periodic purging charges of inert particles containing an amount of carbon equivalent to the normal excess, but carrying no ore. This purge, which may normally require about one-half hour per day of operation, results in a slightly altered temperature gradient, and in the renewed distribution of the alkaline earth chloride from the walls to the inert particles.

Other ores

While I have described my invention with particular reference to chromite ores, it is, of course, to be understood that it is applicable to other chromium containing materials particularly those containing magnesium, calcium or other alkaline earth metal oxides or other materials wherein the formation of molten chlorides such as magnesium chloride presents an accretion or ring formation problem. In addition, the use of carrier particles, although advantageous in many ways, need not be rigidly adhered to and the charge can be an ore-carbon charge or an ore charge in any suitable form with the carbon suitably supplied.

I claim:

1. In a continuous countercurrent process for chlorination in a vertical column of a chromite ore containing silica and magnesia, the steps of maintaining a chlorination zone in an upper portion of said column wherein said ore is reduced and chlorinated and volatilized chlorides are formed, removing said chlorides from an upper portion of said zone to leave a mass of spent ore in said column in another zone below said chlorination zone, maintaining said other zone at a temperature whereat magnesium chloride present solidifies, and maintaining in said other zone a gaseous atmosphere substantially non-adsorbable by said magnesium chloride and which is free of chlorine and hydrogen chloride whereby said magnesium chloride wets the silica present and is carried out of said other zone on the silica.

2. In a continuous countercurrent process for chlorination in a vertical column of a finely divided chromite ore containing silica and materials normally causing agglomeration of the ore, the steps of maintaining a chlorination zone in an upper portion of said column wherein said ore is reduced and chlorinated and volatilized chlorides are formed, removing said chlorides from an upper portion of said zone to leave a mass of spent ore in said column in another zone below said chlorination zone, maintaining said other zone at a temperature whereat chlorinated materials normally causing sintering solidify, and maintaining in said other zone a gaseous atmosphere substantially non-adsorbable by said chlorinated materials and which is free of chlorine and hydrogen chloride whereby said chlorinated materials wet the silica present and are carried out of said other zone on the silica.

3. In a continuous countercurrent process for chlorination of chromite ores containing silica and magnesia wherein the ore is reduced with a carbonaceous material and chlorinated in a column, the steps of admitting oxygen into the column at a point whereat the temperature is below about 711° C. and whereat carbon is present to form a carbon monoxide atmosphere whereby any magnesium chloride present wets the silica, and admitting chlorine at a point in the column above the point of oxygen admission and whereat the temperature is above 850° C.

4. In a continuous countercurrent process for

chlorination of chromite ores containing silica and magnesia wherein the ore is reduced with a carbonaceous material and chlorinated in a column, the step of maintaining a substantially chlorine and hydrogen chloride free gaseous atmosphere non-adsorbable by magnesium chloride in that portion of the column wherein magnesium chloride solidifies whereby liquid magnesium chloride wets the silica.

5. In a continuous countercurrent process for the chlorination of ores containing silica and magnesia wherein the ore is reduced with a carbonaceous material and chlorinated in a column, the steps of admitting air to react with carbon and form a carbon monoxide atmosphere in that portion of the ore column which is at a temperature below the melting point and in the solidification range of magnesium chloride whereby liquid magnesium chloride wets the silica, and admitting chlorine into that portion of the column which is above the melting point of magnesium chloride.

6. In a continuous chlorination-process for an oxidic ore wherein the ore is reduced in the presence of silica in a furnace heated to an elevated temperature with carbon present in admixture with the ore, the ore containing alkaline earth components which are chlorinatable to form liquid alkaline earth chlorides causing cementing of ore particles upon solidification of said liquid chlorides, the steps comprising moving a stream of said ore and carbon through said furnace, introducing an oxygen containing gas into said stream to react with said carbon and form carbon monoxide in the substantial absence of chlorine whereby any alkaline earth chlorides wet the silica, and introducing chlorine into said ore stream at a point whereat carbon monoxide formation is substantially complete.

7. In a continuous countercurrent process for chlorination of chromite ores containing magnesia wherein the ore is reduced in the presence of silica with a carbonaceous material and chlorinated in a heated column, the steps of admitting an oxygen containing gas into the column at a point whereat the temperature is below about 711° C. and whereat the oxygen containing gas reacts to form carbon monoxide with carbonaceous material present, in the substantial absence of chlorine whereby any alkaline earth chlorides wet the silica and are carried out of the column on the silica and admitting chlorine at a point in the column whereat the temperature is above about 850° C. and carbon monoxide formation is substantially complete.

8. In a chromite ore chlorination process, the steps consisting of introducing an ore-carbon stream also containing silica into the top of a vertical shaft furnace, the carbon being present in excess of that quantity required stoichiometrically to reduce the reducible constituents present in the ore, maintaining temperatures in said furnace promoting reduction and chlorination of said ore, introducing chlorine at a point in said furnace which is below the region of maximum temperature and which is at a temperature of about 900° C., and introducing an oxygen containing gas to react substantially completely with carbon present in said stream in that region in said furnace which is below said point of chlorine introduction and below a temperature whereat any alkaline earth chlorides condense whereby said chlorides wet the silica present and are carried out on the silica.

9. In a chromite ore chlorination process, the

steps consisting of introducing an ore-carbon stream also containing silica into the top of a vertical shaft furnace, the carbon being present in excess of that quantity required stoichiometrically to reduce the reducible constituents present in the ore, maintaining temperatures in said furnace promoting reduction and chlorination of said ore, introducing chlorine at a point in said furnace which is below the region of maximum temperature and which is at a temperature of about 900° C., and introducing air to react substantially completely with carbon present in said stream in that region in said furnace which is below said point of chlorine introduction and below a temperature of about 711° C. whereby any alkaline earth chlorides present condense and wet the silica present and are carried out on the silica.

10. In a continuous countercurrent ore chlorination process conducted in a shaft furnace and utilizing an ore-carbon mixture dispersed on relatively massive carrier particles, and separately introduced air and chlorine, the step of periodically purging said furnace with carrier particles substantially free of ore, while maintaining flow of air, chlorine and carbon.

11. The process of claim 4 wherein the gaseous atmosphere is substantially carbon monoxide.

12. The process of claim 4 wherein the gaseous atmosphere is composed largely of nitrogen.

13. In a continuous countercurrent process for chlorination in a vertical column of a chromium containing material including magnesium and silica, the steps of maintaining a chlorination zone in an upper portion of said column wherein said ore is reduced and chlorinated, maintaining said chlorination zone at a temperature sufficiently high to volatilize at least partially metal chlorides formed in said zone and which chlorides pass off as volatilized chlorides from an upper portion of said column to leave a spent ore mass in said column in another zone below said chlorination zone, maintaining said other zone at a temperature whereat magnesium chloride solidifies, and maintaining a chlorine and hydrogen chloride free atmosphere in said other zone which is substantially non-absorbable by said magnesium chloride whereby the magnesium chloride is carried out on the silica.

14. In a continuous countercurrent process for chlorination in a vertical column of a chromium containing material including magnesium and silica, the steps of maintaining a chlorination zone in an upper portion of said column wherein said ore is reduced and chlorinated, maintaining said chlorination zone at a temperature between about 850° C. and 1400° C. to volatilize at least partially metal chlorides formed in said zone and which chlorides pass off as volatilized chlorides from an upper portion of said column to leave a spent ore mass in said column in another zone below said chlorination zone, maintaining said other zone at a temperature below about 711° C. and whereat magnesium chloride solidifies, and maintaining a chlorine and hydrogen chloride free atmosphere in said other zone which is substantially non-absorbable by said magnesium chloride whereby the magnesium chloride wets the silica present and is carried out of the column on the silica.

15. In a continuous countercurrent process for chlorination in a vertical column of a chromium containing material including magnesium and silica, the steps of maintaining a chlorination zone in an upper portion of said column wherein

said ore is reduced and chlorinated, maintaining said chlorination zone at a temperature between about 1150° C. and 1400° C. to volatilize at least partially metal chlorides formed in said zone and which chlorides pass off as volatilized chlorides from an upper portion of said column to leave a spent ore mass in said column in another zone below said chlorination zone, maintaining said other zone at a temperature below about 711° C., and maintaining a chlorine and hydrogen chloride free atmosphere in said other zone which is substantially non-absorbable by said magnesium chloride whereby the magnesium chloride wets the silica present and is carried out of the column on the silica.

16. In a process for chlorination in a vertical column of a chromium containing material including silica and at least one alkaline earth component, the steps of maintaining a reduction-chlorination zone in said column wherein reduction and chlorination of chromium and said component occurs at a temperature between about 850° C. and 1400° C., and maintaining, in another zone in said column below said chlorination zone, a temperature below about 711° C. and a chlorine and hydrogen chloride free atmosphere substantially non-absorbable by a chloride of said component whereby said component wets the silica present.

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