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3,216,817

## BENEFICIATION OF CHROMIUM ORE

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This invention relates to treatment of chromium ores, and more particularly to new and improved process for beneficiation of chromium ores including the low-grade high iron content chromite ores.

Chromium metal and compounds for a wide variety of applications have been of increasing importance and in ever increasing demand. However, the chromium ores which represent the basic source of supply of chromium have become correspondingly a problem of increasing magnitude. As is well known the chromium or chromite ores vary in grade depending largely on iron content which is generally recognized as the more undesirable and difficult to remove impurity. Deposits of chromite ore are found in several locations throughout the world. However, in many of these locations, including the United States, the chromite ore deposits are almost entirely of low grade. Consequently, many countries, including the United States must rely on importation from foreign sources for the higher, so-called metallurgical grade chromium ores which can be processed by known commercially practical methods. Thus, many countries, like this country, must endure the added inconvenience and expense of large-scale importation even though they have available extensive deposits of chromium in the form of the lower grade ores. Additionally, the rapidly changing world situation has made the future of foreign sources of supply uncertain and this, in addition to its potential severe consequences, has already caused extensive and expensive stockpiling of chromium ores as insurance against possible future unavailability. Moreover, the supply of the higher grade ores is becoming short even in those locations having the abundant deposits in the past making the need for development of a successful process for upgrading the low grade ores currently imperative.

The problem with the lower grade chromite ores has been reduction of the high iron content to a desired low level by an economic and commercially practical process. Some beneficiation can be achieved by conventional chromite upgrading procedures but the product is not sufficiently low in iron content to meet the requirements for modern refractory applications let alone suitable for metallurgical use such as for production of chromium metal where a substantially iron-free chromium ore is desired. The problem of beneficiating the low grade chromite ores to obtain the required high chromium to iron ratio has not been overlooked and substantial investigation over the course of the past several years has taken place. Largely, these investigations have been unsuccessful while the others have resulted in methods not practical for large-scale commercial utilization.

One approach to chromite ore beneficiation includes the breaking up of the ore by partial reduction and then leaching the liberated iron with a dilute mineral acid. A major disadvantage of processes of this type is that the leach liquors carry increasing amounts of chromium as attempts are made to increase the chromium to iron ratio. Thus, yields are poor and large amounts of valuable chromium are lost in the leach liquors. Also, if sulfurous or sulfuric acid is used for leaching the product contains sulfur which is difficult to remove and makes the product unattractive for metallurgical use.

Another approach to beneficiation of the low grade chromite ores is chlorination. Processes of this type may

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be divided into two broad categories, namely, processes which are based on complete chlorination of ore including both the iron and chromium content and processes which visualize a selective chlorination of the iron content leaving a beneficiated ore in which the chromium content is substantially unchanged. Most processes are based on complete chlorination and produce gas streams containing the ferric chloride and chromium chloride vapors which must be separated by fractional condensation to recover the chromium values. A process of this general type in which the ore is reacted with carbon and chlorine is the subject of U.S.P. 2,240,345. However, complete chlorination processes usually result in chlorination of other metals in the ore such as aluminum and magnesium and the production of the chlorides of these other metals introduces a number of problems such that this type of process has not gained acceptance.

Selective chlorination of chromium ores to remove only the iron content is rendered difficult because of the affinity of both iron and chromium for chlorine at high temperatures. So difficult indeed that the recent history of the art has recorded statements to the effect that the components of chromite ore are not separable by selective chlorination, Yatlov and Popova, J. Applied Chemistry (U.S.S.R.), 6., 1049 (1933). Moreover, it is recognized that the use of carbon as a reducing agent together with a chlorinating agent such as chlorine offers the possibility of certain practical advantages on which a commercial operation might be based. However, carbon as a reducing agent has been found to more readily effect complete chlorination of the chromite ore constituents and consequently to be less conducive to use in selective chlorination methods. This is confirmed by more recent proposals in the field which have studiously avoided the use of carbon. For example, it has been proposed in U.S.P. 2,277,220 to utilize a combination of chlorine and carbon monoxide to effect selective chlorination. However, the use of carbon monoxide and chlorine for beneficiation of low grade chromite ores has not gained practical acceptance, probably due to low reaction rates and high gas velocities experienced by the prior art workers in this type of process. It has also been stated in U.S.P. 2,752,301 that hydrogen chloride gas may be employed in the absence of carbon to effect selective chlorination of the chromite ores. Processes of this type are also recognized as subject to practical limitations, mainly because of economics and the problems of corrosion control in the utilization of hydrogen chloride. Other prior art workers have also found similar difficulties when attempting to utilize carbon as reducing agent in the utilization of chromite ores. For example, it has been said in effect that experiments with chromite and carbon in separate layers and with suspension of fine powders in a gas stream showed that intimate contact of carbon and ore in the presence of chlorine was always necessary, and extractions by these methods were always wholly unsatisfactory, Maier, "Sponge Chromium," U.S.B.M. Bulletin 436 (1942), p. 49. Despite the recognition of the potential of chlorine and carbon in the beneficiation of chromite ores the prior art has been heretofore unsuccessful in achieving selective chlorination with these materials in a practical manner to produce beneficiated ore having satisfactory high chromium to iron contents. Of perhaps greater significance, the lack of a readily available and practical method of achieving such beneficiation has restrained the utilization of the large amounts of the low-grade chromite ores readily available in the United States and other locations throughout the world.

An object of the present invention is to provide a new and improved process for treatment of chromium ore whereby the chromium ore is beneficiated by selective chlorination of the iron content.

Another object of the invention is to provide a process for treatment of low grade, high iron content chromite ores to produce a beneficiated ore product of high chromium to iron ratio and thus of suitable grade for practical use in both refractory and metallurgical applications.

A further object of the invention is to provide a chromite ore beneficiation process utilizing carbon and a chlorinating agent whereby the iron is selectively and practically entirely removed from the ore to produce a beneficiated ore in which the chromium content is substantially unchanged and recovered in high yield.

A still further object of the invention is to provide a process for treatment of chromium ores including the low grade chromite ores whereby the chromium ore may be beneficiated in a practical, efficient and economic manner utilizing carbon and chlorine to selectively remove iron and produce a high quality beneficiated ore in which the chromium is recovered in high yield.

Other objects and advantages will be evident from the following description of the invention.

It has been found in accordance with the invention that chromium ores including the low grade high iron content chromite ores may be beneficiated in a highly practical and efficient manner involving selective chlorination and removal of iron in the ore in the presence of carbon by a process which comprises subjecting solid reactants including chromite ore and carbon to reaction in the fluidized state with a gas containing chlorine, desirably in the presence of an excess of both carbon and chlorine, at a temperature regulated below about 920° C., preferably a temperature within the range of 850-900° C., to selectively convert iron oxide in the ore by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from the fluidized reaction mass, and recovering beneficiated chromite ore containing original chromium values in high yield.

The process of the present invention treats the chromium ores in a highly efficient and practical manner utilizing carbon and chlorine gas to selectively remove iron from the ore without any substantial effect on the chromium content which is recovered in high yield in the beneficiated product. Of particular interest is the fact that it has also been found that the process of the invention may be carried out utilizing an excess of both carbon and chlorine over the amounts theoretically required to remove only the iron content of the ore. Under these conditions involving the presence of excess carbon and chlorine it would normally be expected that not only the iron but also substantial amounts of other metal values including chromium would be chlorinated and removed from the ore. Such result has been predicted by the art and even encountered in prior art procedures. However, it has been unexpectedly found that an excess of both carbon and chlorine may be employed in the process of the invention without any substantial negative effect on selectivity and, in fact, these conditions are employed in the more preferred embodiments of the invention to selectively remove iron and beneficiate the chromium ores in a highly effective and efficient manner. Excess carbon is advantageously employed along with oxygen to provide for internal heating of the reaction and it has also been surprisingly found that particularly excellent results are obtained when the oxygen is supplied in large excess amounts with the beneficiation proceeding at exceptionally high and desirable rates. Moreover, so effective is the process of the invention in its selectivity despite use of excess carbon and chlorine that practically the entire iron content of the ore may be removed to produce a product of most any desired low iron content without any substantial loss of chromium values. Thus, the chromium ore may be readily beneficiated to less than 3% residual iron, and much lower, with chromium to iron ratios in the product being as high as at least 20:1, and, if desired, up to 50:1 and even higher. Recovery of chromium in the beneficiated ore is generally at least about a high 95%, more usually at least about 98%.

The process of the invention is applicable to the selective removal of iron from chromium ores of widely varying chromium and iron contents. Generally, any noritic chromium ore may be beneficiated with substantially equal effectiveness by the process of the invention. The chromium or chromite ores usually contain about 35 to 55% chromium and about 15 to 25% iron (total as Fe) together with other metal values such as aluminum, magnesium, manganese, nickel and vanadium along with varying amounts up to 8% of silica material. It is generally desirable but not absolutely necessary that the chromium ores prior to beneficiation be concentrated by known procedures which usually control the content of silica material within the range of about 0 to 3%. The iron content of the noritic ores containing ferrous oxide may also contain substantial amounts of ferric oxide and ores containing widely varying proportions of the ferrous and ferric oxides are effectively beneficiated by the process of the present invention. A particularly outstanding feature of the process of the invention is that it is readily adaptable to the beneficiation of the more intractable high iron content chromium ores such as the low grade chromite ores found in abundant supply throughout the world but heretofore largely unexploited. Analysis of these low grade chromite ores after concentration is typically as follows:

	Percent
Cr <sub>2</sub> O <sub>3</sub> -----	35-50
Iron (total as Fe) -----	18-25
Al <sub>2</sub> O <sub>3</sub> -----	10-20
MgO -----	5-15
SiO <sub>2</sub> -----	0.1-5

In carrying out the invention for beneficiation of chromite ores an intimate mixture of ore and carbon is subjected to the action of chlorine gas in a fluidized bed at a temperature within the range of about 800-920° C. The process may be carried out in a conventional fluidized bed reactor having gas feed inlet in the lower portion and separate discharge outlets in the upper portion of the fluidized bed to separately withdraw the beneficiated product and exhaust gases including by-product ferric chloride vapor. The ore and carbon may be charged to the reactor at any convenient location with bottom feeding of the solids mixture employed in the preferred forms of practice as such introduction has been found to give optimum throughput and a substantial increase in capacity of any given reactor. Recovery of the beneficiated ore product is preferably effected from an upper section of the reactor. The carbon, preferably in the form of coke, is desirably substantially greater in particle size than the chromium ore. By employing coke in the form of particles at least 4 times greater in size than the particle size of the ore a number of processing advantages may be realized. For example, in the preferred embodiments employing excess carbon the beneficiated ore may be discharged along with larger carbon particles from the reactor and recovered therefrom by simple separation methods. The use of larger carbon particles also substantially reduces tendency of finer carbon to blowover with the by-product ferric chloride vapors and generally forms a fluidized bed particularly suitable for effective beneficiation of the ore. Preferably, the coke is predominantly about 8 up to about 40 times the particle size of the ore. Ratios in excess of about 60 to 1 are less practical although very fine ore accompanying the use of high ratios tends to be rapidly beneficiated without excessive loss by carryover. In practice, the carbon is usually supplied in the form of coke having a particle size within the range of about 5 to 80 Tyler standard mesh, desirably 5-40 standard mesh. Corresponding particle size of the ore in the more practical modes of operation is predominantly between 100 and 400 standard mesh, preferably between about 170 and 400 standard mesh. Hence, a somewhat broader distribution of ore particle size is acceptable. For example, excellent results are obtained when the solids

charged contain essentially all of the coke at about 10-40 standard mesh while the ore particle size distribution is such that all is minus 80 mesh, with 90% minus 100 mesh, about 85% minus 200 mesh and about 20% minus 400 mesh. Employing the chromium ores in the more finely divided forms has a beneficial effect on removal of iron from the ore and enables highly selective beneficiation with the production of a product of exceptionally low iron content. The by-product ferric chloride may be readily recovered by condensation from the exit gas stream by known procedures.

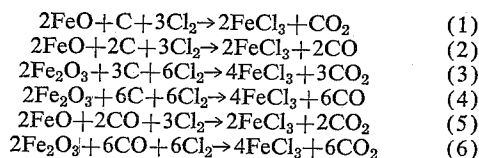
In carrying out the process of the invention to selectively remove iron by chlorination from the chromium ores the reaction temperature within the fluidized bed is regulated within the range of about 800° C. to 920° C. Control of the reaction temperature below 920° C. is particularly important as operation of the fluidized bed above this temperature results in rapidly increasing chlorination and loss of the chromium content of the core. Below a temperature of about 800° C. it has been found that reaction rates and efficiency depreciate to an impractical level. Reaction temperatures within the range of 850-900° C. have been found to give particularly good results with most ores including the low grade high iron content chromite ores.

A feature of the process of the invention is ability to employ large excess amounts of chlorine without resulting in any substantial chlorination of the chromium content of the ore. Under the more preferred conditions of operation in the presence of excess carbon the control of chromium chlorination remains so effective that the amount of chlorine employed may be increased to as much as a 100% excess, and even more. Thus, the actual amount of chlorine employed in the process may be widely varied. As chlorine utilization or efficiency within the bed does not usually reach 100% it is generally desirable to employ at least a 10% excess of chlorine for optimum efficiency in normal operation at the lower chlorine levels. It has been found that a strong correlation exists between the amount of chlorine employed and the residual iron content of beneficiated ore, the larger amounts of chlorine producing the lower iron contents in the product. Under the more preferred conditions of operation a chlorine excess of about 10-80% may be employed to produce a beneficiated product containing less than about 3% residual iron. A chlorine excess of about 25-65% is usually employed under preferred conditions when it is desired to reduce the residual iron content of the product to less than about 2%. It will be noted that ability to employ widely varying amounts of chlorine not only gives the process of the invention a great deal of flexibility, but also provides an effective and efficient method of controlling product quality in terms of residual iron content at most any desired level.

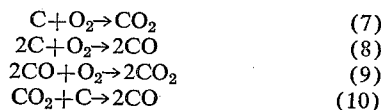
The amount of carbon required to selectively remove only the iron from chromium ores will vary somewhat depending on iron content of the particular ore and the relative amounts of iron present in the ferrous and ferric oxide forms. Generally, a carbon to ore ratio of about 1 to 30-35 represents the theoretical carbon required to convert the iron oxide content of most chromium ores to ferric chloride, based on the formation of a by-product carbon dioxide. While substantial beneficiation may be achieved employing theoretical amounts of carbon it has been found contrary to expectation that excess carbon may be employed without adversely affecting selectivity of the chlorination. Excess carbon may be employed in substantial amounts and used to advantage in practice of the invention. A number of the advantages derived from the use of excess carbon are most effectively realized in conjunction with internal heating of the reactor. Generally, the reaction of carbon and chlorine with the iron content of the noritic ores to produce ferric chloride is exothermic and produces substantial amounts of heat which contribute to maintenance of

temperature conditions within the fluidized bed. However, the reaction is generally not self-sustaining, and loss of heat by radiation is difficult to avoid. Additional heating is therefore usually required to maintain the desired temperature conditions within the bed. The addition of heat to the fluidized bed may be accomplished in several ways including external heating, preheating of reactants including the solids fed to the reactor, and internal heating based on burning of excess coke within the bed. In general, the addition of heat solely by external heating or preheating of reactants, or by a combination of these methods, is less practical from an economic standpoint than internal heating. The use of excess amounts of carbon in the process of the invention provides a readily available means for internal heating and may be employed for such purpose without adversely affecting operation. Thus, while other methods of supplying heat may also be used, it is particularly desirable to supply at least a portion of the additional heat requirements by combustion of carbon within the fluidized bed reactor. In the better forms of practice the desired temperature conditions are maintained by supplying essentially all additional heat requirements by internally heating utilizing excess carbon within the bed.

In practice of the invention in its more preferred embodiments including internal heating, the process is initiated by charging coke of the desired size to a fluidized bed reactor. The charged coke is fluidized with an oxygen containing gas and burned to bring the reactor up to the reaction temperature, preferably 850-900° C. Introduction of the solids feed mixture of ore and coke in the desired proportions is then commenced and beneficiation started by introducing a gas containing chlorine and oxygen into the reactor. The actual ratio of carbon to ore in the solids feed may depend on several factors including the exothermic value of the reaction based on the ore content, the amount of internal heating to be supplied, heat losses from the reactor, and the amount of oxygen in the feed gas. Generally, it is desirably to conduct the reaction in the presence of about a 100% excess of carbon such that the ratio of carbon to ore is at least about 1 to 15. When a substantial portion of the additional heat requirement is to be supplied by internal heating the ratio of carbon to ore is preferably within the range of about 1:10 to 1:1. In situations where total internal heating is employed particularly good results are obtained when the ratio of carbon to ore is within the range of about 1:6 to 1:2. The amount of oxygen required to provide for substantial internal heating of the reaction is usually about 0.1-1.4 mol per mol of theoretical chlorine, i.e. the amount of chlorine required to convert the iron content of the ore to ferric chloride. It has been found that increasing the amount of oxygen in the feed gas above a ratio of about 1 to 1 mol per mol of theoretical chlorine results in a surprising and sharp increase in reaction rates with residence time of the ore in the reactor reduced from hours to a matter of only a few minutes. A definite explanation for this highly desirable result can not be given with absolute certainty as a number of reactions may take place during beneficiation, as indicated by the following equations:



Oxygen may also react with carbon according to the following equations:



It will be noted that the iron oxide content of the ore may be converted to ferric chloride by reaction with carbon according to Equations 1-4, inclusive, and by reaction with carbon monoxide according to Equations 5 and 6. In the absence of oxygen the beneficiation must proceed to some extent by direct attack of carbon on the iron oxide according to Equations 1-4, inclusive. Carbon monoxide formed by the reactions of Equations 2 and 4 in such a case might also contribute to the beneficiation according to the reaction of Equations 5 and 6. Carbon in the presence of oxygen may react according to Equations 7-10, inclusive. However, under the temperature conditions involved in the process of the invention the reactions of Equations 8 and 10 predominate over the reactions of Equations 7 and 9 which are not favored thermodynamically. Thus, the oxygen supplied for internal heating is converted largely to carbon monoxide which rapidly increases in concentration substantially proportionally with increasing amounts of oxygen. The sharp increase in reaction rates when large amounts of oxygen are employed would logically appear due to substantial reduction of the iron oxide by carbon monoxide. Normally, however, the reaction of the iron oxide with carbon monoxide as shown by Equations 5 and 6 is very slow. The high reaction rate obtained in the use of large amounts of oxygen is therefore unexpected and possibly caused by one or more factors such as a high excess concentration of carbon monoxide, or the formation of a highly activated carbon or carbon monoxide, or even possibly due to a combined effect of carbon monoxide and carbon. In the more preferred embodiments of the invention particularly excellent results are obtained when the ratio of oxygen to the theoretical chlorine is regulated within the range of about 1:1 to 3:1.

In practice, the composition of the feed gas as well as the amounts of chlorine and oxygen may be varied depending upon desired operation conditions and the requirement for maintaining the solids reactants in the fluidized state above the incipient velocity of the bed. The oxygen introduced into the reactor may be commercial oxygen or supplied from ordinary air. When employing ordinary air, nitrogen and other inerts in the air act as diluents. If the oxygen supplied by the air is less than desired, it may be readily made up by the addition of oxygen from other sources, such as commercial oxygen. If the amount of oxygen supplied by the use of ordinary air exceeds requirement, the desired level may be easily obtained by addition of diluents such as nitrogen. The rate of feed of the gas to the fluidized bed is of course largely dependent on maintaining the desired equilibrium conditions and proper control over the fluidized solids including both reactants and product. Velocity set too low above the incipient velocity tends to lead to entrainment while too high a velocity reacts in undesired blow-over of reactants. The superficial velocity of the gas above the incipient bed velocity may of course vary over a fairly wide range depending on several factors involved in operation of the process including the size and relative proportioning of the ore and coke and reaction rates. Under the more preferred conditions of operation a superficial velocity of about 50-400% in excess of the incipient velocity has been found to give good results permitting maximum recovery of the beneficiated ore and good control of the process.

Recovery of the beneficiated ore product is facilitated by the use of excess carbon having particle size substantially greater than that of the ore. During operation of the process employing excess carbon the larger carbon particles are generally depreciated only somewhat in size. The mixture of beneficiated ore product and carbon discharged from the fluidized bed therefore contains the carbon particles at a size still substantially larger than that of the finely divided beneficiated ore product which may be readily separated from the carbon and recovered by simple conventional methods such as screening,

air classifying, or gravity separation. In this manner a high degree of separation of the ore product and carbon may be obtained such that the beneficiated ore product contains less than about 1.0% carbon which is desirable for certain applications in which the ore might be employed.

The process of the present invention is particularly outstanding in its ability to beneficiate chromium ore on a practical, highly efficient basis such that chromium recovery in the product is at about 95%, and more usually of the order of about 98%. The ferric chloride recovered as by-product is of good purity and contains less than about 2% by weight aluminum chloride and less than about 3% chromium chlorides. Under optimum conditions the amount of chromium chlorides in the ferric chloride by-product is less than 2%. The ferric chloride recovered is therefore suitable for conversion to ferric oxide useful in manufacture of magnetic and electrical devices. If desired, chlorine gas produced on conversion of the ferric chloride to ferric oxide may be recovered and reused in the process. In carrying out the invention most any degree of beneficiation may be accomplished. Beneficiated ore is readily obtained having chromium to residual iron ratios of at least about 20 to 1, or less than about 3% iron, more usually a ratio of chromium to iron of about 40:1 to 50:1, and even higher. The highly beneficiated chromium ores obtained by the process of the invention are suitable for use as refractory composition per se or after admixture with other chromium values, and are also particularly suited for further treatment for production of chromium metal and compounds of chromium.

The following examples in which percentages are by weight demonstrate the practice and advantages of the present invention.

#### Example I

A laboratory fluidized bed reactor having 2 inch internal diameter and length of 40 inches was employed to beneficiate a Transvaal chromite ore concentrate having the following analysis:

	Percent
Cr <sub>2</sub> O <sub>3</sub> -----	47.12
Total iron as Fe -----	18.69
Al <sub>2</sub> O <sub>3</sub> -----	15.80
MgO -----	11.40
SiO <sub>2</sub> -----	0.51

The ore was screened to pass an 80 mesh screen and remain on a 200 mesh screen with 33% plus 100 mesh. The ore was admixed in a rotating drum mixer with coarse coke having a particle size such that about 100% passed a standard 40 mesh screen and was retained on a 100 mesh screen. Ratio of ore to coke was 97.2 to 2.8 by weight such that the ratio of iron content of the ore (expressed as Fe) to coke was about 6.5 to 1. The mixture contained approximately the theoretical amount of carbon required to convert the iron oxide content of the ore to ferric chloride. Over the course of about 72 hours the mixture of ore and coke was continuously fed to the fluidized bed at an average rate of about 200-300 grams per hour. The starting bed consisted of 1515 grams of a beneficiated ore containing 63.13% chromic oxide and 0.92% iron as Fe. The fluidized bed of reactants was maintained by the introduction of gas at the bottom of the bed at a rate of about 4.17-4.20 Standard Cubic Feet per hour. The gas employed to maintain the fluidized bed was composed of chlorine in amounts regulated between about 1.12-2.65 s.c.f./hr. with the balance being nitrogen. Average chlorine rate was 1.57 s.c.f./hr. The chlorine gas continuously introduced into the fluidized bed represented an excess of about 25-67% over theoretical required for conversion of the iron content of the ore to ferric chloride. Reaction temperature in the fluidized bed was regulated between about 800-925° C. and maintained solely by external heating. Reaction temperature

was measured by use of thermocouples located inside the reactor and represented the average of readings taken at lower intermediate and upper sections of the fluidized bed. Maximum variation among the temperature readings in the different sections was about 10° C. From a 1 inch discharge outlet near the top of the reactor there was continuously discharged a stream containing vapors of metal chlorides formed by reaction of the chlorine with the ore along with extraneous gas including excess chlorine, nitrogen, and less than about 0.25% carbon. Analysis of the by-product metal chlorides showed that ferric chloride was discharged from the reactor at the rate of about 118.5 grams per hour, aluminum chloride at a rate of about 4.8 grams per hour, and chromium chlorides at a rate of only about 1.5 grams per hour. Based on total metal chlorides in the vapor the amount of chromium chlorides was a low 1.27% indicating virtually complete selective chlorination in the fluidized reactor. From a separate discharge outlet at the bottom of the reactor there was continuously discharged beneficiated ore at an average rate of about 198.8 grams per hour. The beneficiated ore was found to have the following analysis:

	Percent
Cr <sub>2</sub> O <sub>3</sub> -----	63.4
Iron (total as Fe) -----	0.8
Al <sub>2</sub> O <sub>3</sub> -----	21.6
MgO -----	14.0
SiO <sub>2</sub> -----	0.9

The product contained less than 0.1% carbon. Overall material balance showed a chlorine utilization of about 62%. Iron volatilization was a high 95.5% and chromium recovery after correction for mechanical losses a high 99.4%. Degree of beneficiation obtained by the invention process as shown by the product analysis was such that the product exhibited a desirably high ratio of chromium to iron of about 54.2 to 1. These results were obtained with a high iron content ore of the type found most difficult in the past to treat for successful removal of the iron.

#### Example II

A fluidized reactor of pilot plant scale having 12 inch internal diameter and length of 24 inches was employed to beneficiate a Transvaal chromite ore concentrate having analysis similar to the ore treated in Example I. The ore was finely divided and had a standard screen analysis such that 90% was minus 100 mesh, and 20% minus 400 mesh. The ore was admixed in a ribbon blender with coarse coke having a particle size such that about 85% passed a standard 10 mesh screen and 100% was retained on a 20 mesh screen. Ratio of coke to ore was about 1 to 3 by weight. The mixture contained coke in about a 800% excess of the amount theoretically required to convert the iron content of the ore to ferric chloride. Over the course of about 140 hours the mixture of ore and coke was continuously fed to the top portion of the fluidized bed at an average rate of about 30 pounds per hour. The fluidized bed of reactants weighing about 70 pounds was maintained by the introduction of gas at the bottom of the bed. The feed gas employed to maintain the fluidized bed was composed of about 11% chlorine, 21% oxygen, and 68% nitrogen. The gas was prepared by mixing of chlorine gas with nitrogen and oxygen gases. Velocity of gas through the fluidized bed was about 0.8 ft./sec. representing a superficial velocity of about 400% over the approximated incipient fluidizing velocity of about 0.2 ft./sec. The chlorine gas continuously introduced into the fluidized bed represented an excess of about 47% over theoretical required for conversion of the iron content of the ore to ferric chloride. Reaction temperature in the fluidized bed was about 860–870° C. and maintained solely by the burning of excess coke within the bed and without external heating. Reaction temperature was measured by use of thermocouples

located about 2–3 inches inside the reactor and represented the average of readings taken at lower, intermediate and upper sections of the fluidized bed. Maximum variation among the temperature readings in the different sections was about 10° C. From a 2 inch discharge outlet near the top of the reactor there was continuously discharged a gas stream containing vapors of ferric chloride formed by reaction of the chlorine with the ore along with extraneous gas including excess chlorine, nitrogen, CO<sub>2</sub>, CO and some COCl<sub>2</sub> resulting from combination of CO and Cl<sub>2</sub> as the gases cooled. This gas stream was scrubbed by countercurrent contact with water to remove the metal chloride by-products including ferric chloride. Analysis of the by-product ferric chloride showed less than 1% chromic chloride based on ferric chloride indicating virtually complete selective chlorination in the fluidized reactor. From a separate 2 inch diameter discharge outlet in an upper portion of the reactor there was continuously discharged a solids mixture containing coke and beneficiated ore. The solids were discharged from the reactor at an average rate of about 13.3 pounds per hour. Residence time was of the order of five minutes. The product stream was scalped on an 80 mesh screen to separate the larger coke particles from the smaller particles of beneficiated ore. The beneficiated ore (–80 mesh material) was found to have the following analysis:

	Percent
Cr <sub>2</sub> O <sub>3</sub> -----	60.5
Iron (total as Fe) -----	2.0
Al <sub>2</sub> O <sub>3</sub> , MgO, SiO <sub>2</sub> -----	35.9
C -----	1.0

Degree of beneficiation obtained by the invention process as shown by the product analysis was such that the product exhibited a desirably high ratio of chromium to iron of about 20.5 to 1. These results were obtained with a high iron content ore of the type found most difficult in the past to treat for successful removal of the iron.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

#### We claim:

1. The process for beneficiation of chromite ore which comprises subjecting chromite ore and carbon to reaction in the fluidized state with a gas containing chlorine at a temperature regulated above 800° C. and below about 920° C. to selectively convert iron oxide in the ore by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from the fluidized reaction mass, and recovering beneficiated chromite ore containing original chromium values in high yield.
2. The process of claim 1 in which the temperature is regulated between about 850–900° C.
3. The process of claim 1 in which the chlorine gas is supplied in at least about a 10% excess over the amount theoretically required to convert the iron content of the ore to ferric chloride.
4. The process of claim 1 in which the chromite ore is a low grade high iron content chromite ore containing 35–50% chromic oxide and about 18–25% iron (total as Fe).
5. The process for beneficiation of chromite ore which comprises subjecting chromite ore to reaction in the fluidized state with an excess of carbon and with a gas containing at least about a 10% excess of chlorine over the amount theoretically required to convert iron content of the ore to ferric chloride, at a temperature regulated above 800° C. and below about 920° C. to selectively convert iron oxide in the ore by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from the fluidized reaction mass, and recovering beneficiated chromite ore containing original chromium values in high yield.

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6. The process of claim 5 in which the carbon in the fluidized reaction mass is present in at least about a 100% excess over the amount theoretically required for conversion of the ferric oxide to ferric chloride.

7. The process for beneficiation of chromite ore which comprises subjecting finely divided chromite ore to reaction in the fluidized state with carbon and a gas containing at least a 10% excess of chlorine over the amount theoretically required to convert the iron oxide content of the ore to ferric chloride, the carbon being supplied in the form of coke having particle size at least about 4 times greater than the particle size of the ore, at a temperature regulated above 800° C. and below about 920° C. to selectively convert iron oxide in the ore by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from the fluidized reaction mass, and recovering beneficiated chromite ore containing original chromium values in high yield.

8. The process of claim 7 in which the carbon is present in at least about a 100% excess and the particle size of the carbon is predominantly within the range of 5 to 80 Tyler standard mesh.

9. The process of claim 7 in which the carbon is present in at least about a 100% excess, the particle size of the carbon being at least about 8 times the particle size of the ore and predominantly within the range of 5-40 Tyler standard mesh.

10. The process for beneficiation of chromite ore which comprises subjecting chromite ore to reaction in the fluidized state with an excess of both carbon and chlorine over the amounts theoretically required to convert the iron oxide content of the ore to ferric chloride, adding ore and carbon to the fluidized reaction mass, introducing chlorine and an oxygen-containing gas into the fluidized reaction mass, supplying heat to said reaction by combination of oxygen with excess carbon while simultaneously regulating the temperature within the range of about 800-920° C. to selectively convert iron oxide in the ore by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from the fluidized reaction mass, and recovering beneficiated chromite ore containing original chromium values in high yield.

11. The process of claim 10 in which the ratio of carbon to ore is at least about 1 to 10 and the chlorine is supplied in at least about a 10% excess over the amount theoretically required to convert the iron oxide content of the ore to ferric chloride.

12. The process of claim 10 in which the ratio of carbon to ore is at least about 1 to 10, the carbon having particle size at least about 4 times greater than the ore, and the beneficiated ore discharged from the fluidized reaction mass along with coke predominantly larger in size than the beneficiated ore.

13. The process of claim 10 in which the carbon and oxygen supplied are at least sufficient to maintain the

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reaction essentially solely by heat of the reaction and combustion of excess carbon within the fluidized mass.

14. The process of claim 10 in which the ratio of oxygen to theoretical chlorine is at least about 1 to 1.

15. The process for beneficiation of chromite ore which comprises maintaining a fluidized bed of reactants including chromite ore and carbon, adding to said bed carbon and finely divided chromite ore having particle size relative to each other such that the carbon is predominantly at least about 4 times greater than the particle size of the chromite ore, the amount of carbon and ore being regulated such that the ratio by weight of carbon to ore is greater than about 1 to 10 to provide excess carbon over that theoretically required to convert the iron content of the ore to ferric chloride, introducing a gas containing at least a 10% excess of chlorine and oxygen in an amount such that the ratio of oxygen to theoretical chlorine is at least about 1 to 1, supplying heat internally to said fluidized bed of reactants by combination of oxygen with excess carbon while simultaneously regulating the temperature in said fluidized bed within the range of about 800° C. to 920° C. to selectively convert iron oxide by reaction with chlorine gas to ferric chloride, releasing volatile ferric chloride from said fluidized bed, discharging from said bed a mixture of beneficiated ore and carbon in which the carbon particles are predominantly larger in size than the particles of the ore, and separating said carbon from said ore to recover beneficiated chromite ore containing original chromium values in high yield.

16. The process of claim 15 in which the reaction temperature is 850-900° C.

17. The process of claim 15 in which the ratio by weight of carbon to ore is within the range of about 1:6 to 1:2 and amount of oxygen within the range of about 1:1 to 3:1 mols per mol of theoretical chlorine.

18. The process of claim 15 in which the chromite ore and carbon are added at the bottom of the fluidized bed as a mixture containing carbon having particle size predominantly in the range of about 5-40 Tyler standard mesh.

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