

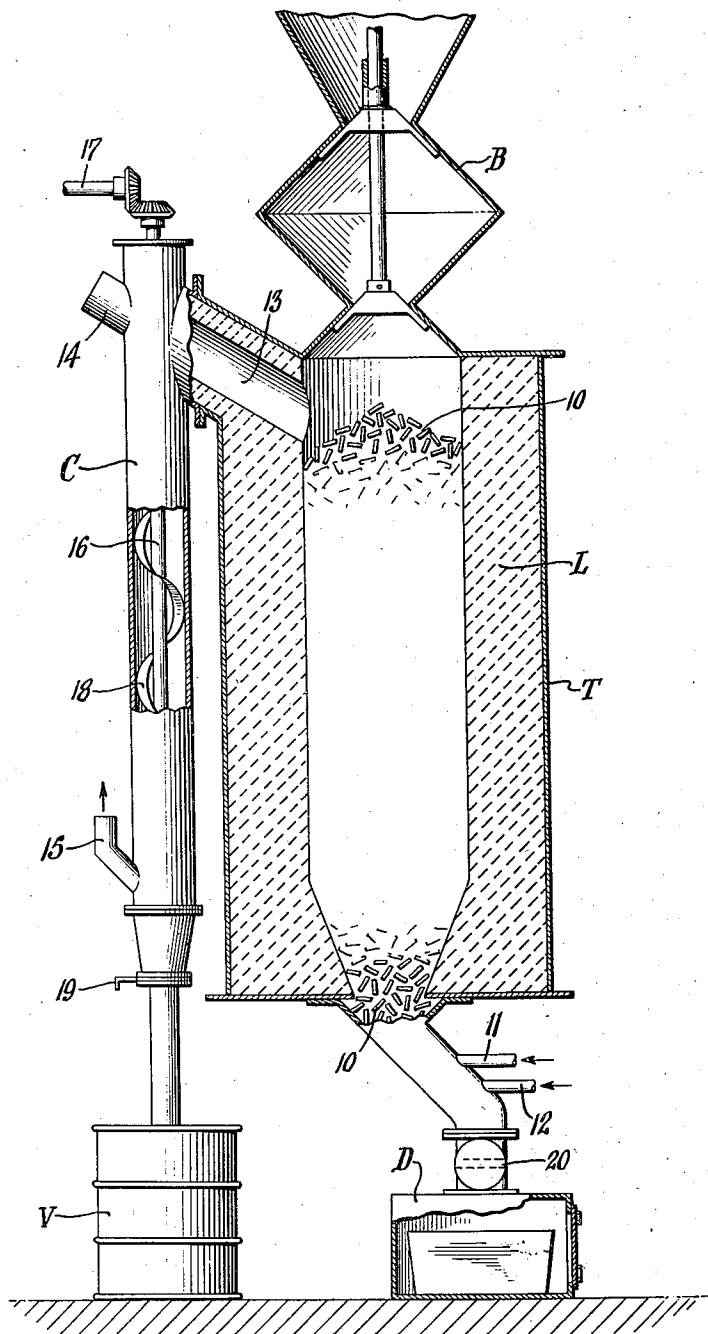
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ORE TREATMENT

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ORE TREATMENT

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5 Claims. (Cl. 75—1)

This invention relates to methods of treating materials containing oxides of iron and chromium, for instance chromite, for the principal purpose of raising the ratio of chromium to iron in such material.

There exist large deposits of chromite-bearing ore in which the ratio of chromium to iron is so low that the ore is considered to be of an inferior grade. In general, if the ratio of chromium to iron is less than three to one, the ore is ill suited to important uses now made of high grade ores, for instance the manufacture of ferrochromium containing 65% to 72% chromium. It is important to the producer and consumer alike that there be available an economical method of treating the low grade ore to raise the ratio of chromium to iron to at least three to one, and it is a specific object of this invention to provide such a method.

A more general object of the invention is to provide a method of raising the ratio of chromium to iron in a wide variety of materials containing oxides of both chromium and iron.

A further object is to remove, from materials containing oxides of both chromium and iron, substantial amounts of iron but only insignificant amounts of chromium.

Other objects will be apparent from the following description and the accompanying drawing in which the single figure is a diagrammatic representation in cross-section of a suitable furnace for use in practicing the invention.

In accordance with the invention, material containing oxides of both chromium and iron is treated with carbon monoxide and an agent selected from the group consisting of chlorine, sulfur chloride, and mixtures of chlorine with sulfur chloride, at an elevated temperature above about 600° C. The temperature employed should not be so high that any substantial amounts of chromium chlorides are formed; ordinarily this temperature will be below 850° C., but the upper temperature limit varies with different conditions, for example, of gas velocity, gas concentration, and pressure, and in some instances may be 900° C. or higher. At the proper temperatures, iron oxide in the ore is converted to iron chloride, most of which is volatilized, but no substantial part of the chromium is converted to the chloride.

The material to be treated, chromite ore for example, is crushed, for instance to pass through an 8 mesh screen (2.4 mm. openings). It may be finely ground, for instance to such a particle size that most of the material will pass through a 100 mesh screen (0.15 mm. openings). In either case, the crushed or ground material may be pressed into the form of pellets or briquets, using water or other suitable binder, or the ore may be treated in the loose, unbonded condition. It

is best to dry or calcine the material before treating it. The calcination will drive off water and will harden the briquets if the material is used in that form.

5 The carbon monoxide and chlorine, sulfur chloride, or chlorine-sulfur chloride mixture may be passed over or through the material to be treated. It is preferred to use an excess of at least one of the gases, or to use a diluent, or both an excess and diluent, to aid in flushing out the volatilized iron chloride and to carry such chloride out of the treating chamber into a suitable condenser where it may be condensed as a solid.

10 The carbon monoxide and chlorine (or sulfur chloride or chlorine-sulfur chloride mixture) may be used in any appropriate proportions, for instance equal volumes of chlorine and carbon monoxide. Other gases, such as nitrogen and carbon dioxide, may be present with the chlorine and carbon monoxide. Carbon monoxide containing a substantial proportion of nitrogen may be prepared by the combustion of coke with air in a gas generating chamber. The use of carbon monoxide generated in this way is preferred.

15 Any by-product or industrial gas containing an appreciable proportion of carbon monoxide may be used in the process of this invention, although it should be noted that hydrogen or hydrogen compounds detrimentally affect the efficiency of the operation by contributing to the formation of hydrogen chloride. Nitrogen and carbon dioxide are not harmful to the reaction and may even be beneficial when functioning as diluents.

20 The treatment may be carried out in any suitable vessel, for example, a retort, sagger, tube or shaft furnace. If a shaft furnace or a similar type of apparatus is used, the treatment of successive charges of ore may be made continuous. In such case, the effluent gases may be readjusted as to composition after the removal of at least the major part of the ferric chloride and then recycled. Preferably, the reaction vessel is well insulated to prevent loss of heat by radiation. The reaction is self-sustaining, and after the vessel is brought to the necessary temperature no heat need be added unless there are substantial losses of heat.

25 The single figure of the drawing diagrammatically illustrates a furnace suitable for use in practicing the invention. A vertical tube T in which the charge 10 is held is provided with a refractory lining L. A double bell charging device B adapted to charge the furnace without opening it to the atmosphere is mounted on top of the tube T, and a device D into which treated material is discharged through a valve 20 is provided at the bottom of the tube T. A carbon monoxide inlet 11 and a chlorine inlet 12 are provided for admitting gases to the interior of the tube T. From the top of the tube T a flue

13 leads into a condenser C provided with a "clean out" 14, an exhaust gas outlet 15, a shaft 16 driven by a driving mechanism 17 and provided with a helical scraping means 18 for removing condensed ferric chloride from the condenser C. Ferric chloride is condensed from the gas emanating from the tube T in the condenser C and is discharged into a container V through a valve 19.

In using this type of furnace, the reaction is initiated by the combustion of fuel gas in the charged furnace. When the proper temperature is reached, chlorine is admitted to the furnace through the chlorine inlet 12, and a mixture of carbon monoxide and nitrogen is admitted through the inlet 11. The heat in the furnace is maintained by the reaction. The temperature may be regulated by adjusting the carbon monoxide-nitrogen mixture. Vapors containing ferric chloride are withdrawn through the flue 13 into the condenser C in which ferric chloride is recovered and from which ferric chloride may be removed intermittently or continuously. The exhaust gas from the condenser C may be adjusted as to composition and recycled in known manner or may be wasted. The treated material is collected in the device D. The furnace may be operated continuously, or the operations may be of the batch type.

If desired, external heating means, for example a muffle equipped with a gas burner, may be used to heat the furnace initially.

The principles of the invention are illustrated in the following specific examples. A low grade chrome ore containing 30.2% chromium and 18.5% iron (ratio Cr:Fe=1.6:1) was ground to pass a 100 mesh screen, and formed into briquets, using water as a binder. In a test running 2.8 days, 2,796 pounds of dried briquets were fed, portionwise, into the top of a vertical tube furnace eight feet in height, and fourteen inches in diameter. The furnace was maintained at an average temperature of approximately 715° C. in the reaction zone. Into the bottom of the tube was fed a mixture of 650 pounds of chlorine, 375 pounds of carbon monoxide, and 945 pounds of nitrogen. (CO and N₂ obtained from the combustion of coke in air.) From the bottom of the tube were withdrawn 1,837 pounds of briquets containing 32.9% chromium and 8.9% iron (ratio Cr:Fe=3.7:1) and 643 pounds of briquets containing 16.5% iron. The total weight of briquets recovered was 2,480 pounds, having an average composition of 32.7% chromium and 10.6% iron (ratio Cr:Fe=3.1:1). 533 pounds of crude ferric chloride containing 0.13% chromium were condensed and recovered. The chlorine efficiency (based on FeCl₃ removed) was 75.7%.

In another test using the same kind of ore, 150 pounds of briquets were calcined and fed as a batch into the top of a well-insulated vertical tube furnace of the type shown in the drawing. The reaction was started by burning carbon monoxide and air within the furnace in such manner that the combustion occurred within the charge. After obtaining a temperature of about 800° C. the air was shut off, and chlorine was fed into the furnace at a rate of about one-half cubic foot per minute, together with a carbon monoxide-nitrogen mixture which was fed at a rate of about three cubic feet per minute. The carbon monoxide-nitrogen mixture contained 25.9% car-

bon monoxide, 68.4% nitrogen, the remainder principally carbon dioxide. The temperature remained at about 800° C. to 850° C. for about 8½ hours. A total of 32 pounds of chlorine, 26 pounds of carbon monoxide and 70 pounds of nitrogen was fed into the furnace. A representative portion of the treated material contained 36.2% chromium and 4.4% iron (ratio Cr:Fe=8.2:1). The ferric chloride formed in the reaction was condensed from the exit gases. No chlorine was detectable in the exit gases by the usual tests, and very little carbon monoxide was present. The chromium recovery based upon an aggregate sample of the entire mass discharged was 100%.

I claim:

1. Method of removing iron from a material containing oxides of both chromium and iron which comprises subjecting such material, at a temperature above about 600° C., but below the temperature at which substantial amounts of chromium chlorides are formed, to the action of a gaseous mixture consisting essentially of carbon monoxide, a chlorinating agent selected from the group consisting of chlorine, sulfur chloride, and mixtures thereof, and a diluent gas substantially free from hydrogen, whereby iron oxide is converted to iron chloride but no substantial proportion of chromium oxide is attacked; and volatilizing and removing at least the major portion of the iron chloride so formed.

2. Method as claimed in claim 1 in which the chlorinating agent employed is chlorine and the diluent gas is carbon monoxide in excess of that which will react with said material.

3. Method of removing iron from a chromite ore which comprises subjecting finely ground ore, at a temperature between 600° C. and 900° C., to the action of a stream of gas consisting essentially of chlorine, carbon monoxide, and a diluent gas substantially free from hydrogen, whereby to form iron chloride without attacking any substantial proportion of chromium oxide; volatilizing and removing at least the major portion of the iron chloride so formed; and continuing the treatment until the ratio of chromium to iron of said ore has been raised substantially.

4. Method of removing iron from a chromite ore containing chromium and iron in a ratio lower than 3 to 1 which comprises passing through the ore, ground sufficiently fine to pass a 100 mesh screen (0.15 mm. openings) and at a temperature between 600° C. and 900° C., a stream of gas essentially comprising chlorine, carbon monoxide, and a diluent gas substantially free from hydrogen, whereby to form iron chloride but no substantial proportion of chromium chloride; volatilizing and removing in said stream the iron chloride so formed; and continuing the treatment until the ratio of chromium to iron of said ore is at least 3 to 1.

5. Method of removing iron from a chromite ore which comprises finely grinding such ore; forming the ground ore into briquets; and subjecting such briquets, at a temperature between about 600° C. and 900° C., to the action of a stream of gas essentially comprising chlorine, carbon monoxide, and a diluent gas substantially free from hydrogen, whereby to form iron chloride; and removing in said stream the iron chloride so formed.

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