

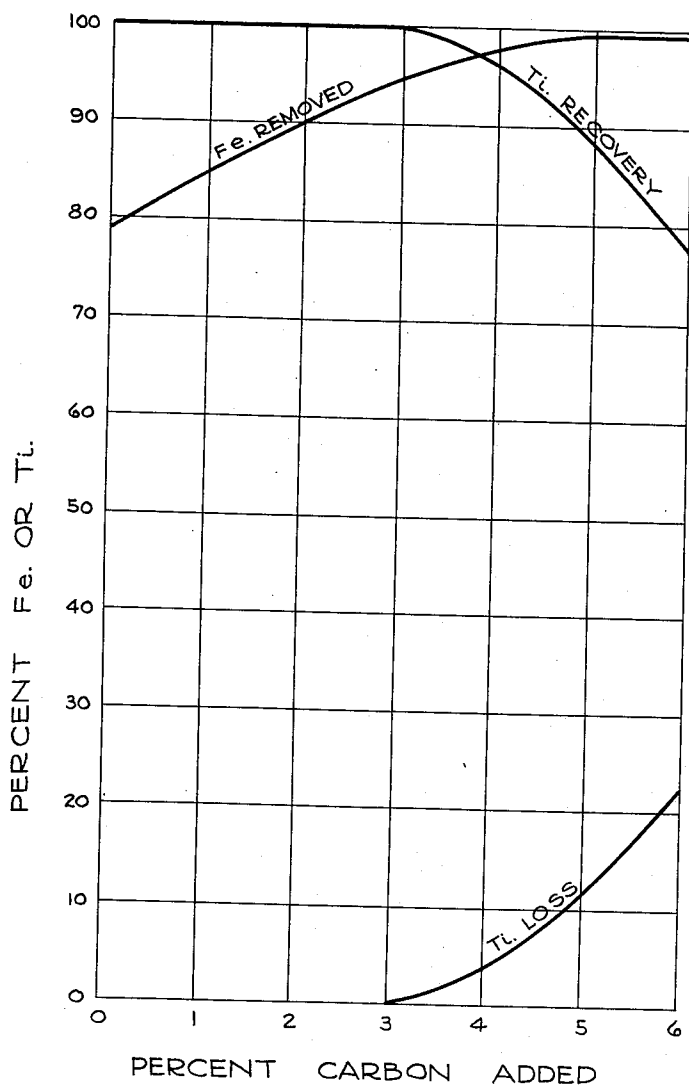
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TREATMENT OF TITANIUM ORES

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CHLORINATION OF ILMENITE AT 980° C.
REMOVED Fe. & Ti. WITH VARYING CARBON CONCENTRATION

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TREATMENT OF TITANIUM ORES

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This invention relates to the production of titanium compounds, in particular titanium tetrachloride and titanium dioxide from iron-titanium ores, such as ilmenite, by chlorination of such ores.

In order to secure titanium dioxide suitable for pigmentary purposes from ferro-titanium ores, it is essential that a careful separation of titanium from iron be secured. Previously, when the recovery of titanium by chlorination has been attempted, considerable difficulty has been encountered in obtaining an iron-free product without substantial loss of titanium since ferric chloride and titanium tetrachloride are both readily volatile at relatively low temperatures. Prior to this invention, the production of a substantially iron-free titanium compound by chlorination of ferro-titanium ores has not been regarded as successful from a commercial standpoint.

We have found that the amount of iron and titanium which may be removed as volatile chlorides from an iron-titanium ore, such as ilmenite, may be effectively controlled by regulation of the amount of a reducing agent, such as carbon, which is in intimate contact with the ore during chlorination. Within the range of temperature which we have found it desirable to operate, we have observed that some iron may be removed as volatile chlorides by chlorination of iron-titanium ores, without substantial volatilization of titanium compounds in the absence of a reducing agent. Such a process can not be used to effectively remove iron from the titanium ore since the iron removal is very incomplete and a considerable quantity of titanium is lost during chlorination. However, we have found that if chlorination of the ore is carried out in the presence of added carbon, more or less intimately intermixed with the ore, further amounts of iron are volatilized and at a certain optimum range of carbon concentrations, the major portion of the iron may be removed without substantial loss of titanium from the ore. When ore-carbon mixtures containing carbon in excess of this optimum concentration range are chlorinated, some quantity of titanium is volatilized as titanium tetrachloride; and, when ore mixtures containing large excesses of carbon are chlorinated, the major portion of the iron and titanium in the ore is thereby removed as volatile chlorides. By chlorination of ore-carbon mixtures in which the carbon concentration approximates the optimum concentration range, previously referred to, we are able to secure a

very effective removal of iron from these ores without removing any substantial proportion of the titanium, leaving a product which is largely titanium dioxide and contains substantially all of the original content of the titanium.

The range of carbon concentrations necessary to secure such a removal of iron with substantially no loss of titanium is dependent, to some extent, upon the relative amounts of iron and titanium in the ore and also upon temperature of operation. Within a temperature range of 700–1150° C., changes in temperature do not appear to require substantial change in carbon concentration but at temperatures below this range slightly increased carbon concentrations may be desirable. In addition, the carbon concentration required may be greatly changed by the presence or absence of oxidizing agents, such as air, oxygen, ozone, etc., which may be used in conjunction with the chlorinating gas. In our copending application Serial No. 205,322, filed April 30, 1938, we have described and claimed the chlorination of iron-titanium ores in the presence of such oxidizing gases. The present invention is directed to the chlorination of such ores in the substantial absence of such oxidizing gases.

The invention will be more fully understood by reference to the following description illustrated by the accompanying drawing in which the figure is a graph, illustrating the effect of varying amounts of carbon upon the amount of iron and titanium which is volatilized by treatment of a mixture of carbon and ilmenite in a stream of chlorine at a temperature of 980° C.

It has been found that most efficient results may be obtained by chlorination at a temperature in excess of 500° C. In general, extreme temperatures result in melting or softening of ores such as ilmenite to the extent that caking or clinkering occurs and proper distribution of the chlorine becomes extremely difficult if not impossible. While chlorination of ilmenite may be secured at temperatures below 500° C. the reaction is very slow and the heat developed during the reaction does not appear to be sufficient to maintain the operating temperature. For most efficient chlorination, we prefer to maintain the temperature of treatment between 700–1150° C. These temperatures appear to permit maximum iron removal with minimum loss of titanium for a minimum period of chlorination.

The graphs in the figure illustrate the variation in the percent of iron and titanium removed as volatile chlorides and the percent of

titanium remaining in the residue, with varying amounts of carbon. The ore treated contained 25.8 percent iron and 35.2 percent titanium. Samples of varying carbon content were prepared by adding finely divided carbon to ground up ore and intimately intermixing to form a product of substantially uniform composition. This composition was mixed with 12 percent by weight of molasses calculated upon the weight of the ore and the mixture briquetted to form briquettes of $\frac{1}{8}$ inch in diameter which were baked at 400° C. to remove volatile hydrocarbons. The baked briquettes were then chlorinated at a uniform rate of 140 liters per minute per kilogram of sample for 5 minutes at 980° C. and the amount of iron and titanium lost determined by analysis. The carbon concentration is expressed in terms of the number of grams of carbon which was mixed with 100 grams of ore, exclusive of the carbon which may be present due to the addition of the molasses. The iron and titanium loss is expressed in terms of a percentage of the amount of iron and titanium, respectively, which was initially in the ore. Thus, it will be seen that, for the particular ore in question, chlorination for 5 minutes at 980° C. in the absence of added carbon resulted in a removal of but 79 percent of the total iron initially present in the ore. In contrast to these results, chlorination of an ore-carbon mixture containing 4 percent of added carbon under the same conditions resulted in removal of 97.5 percent of the iron with a loss of only 3.5 percent of the titanium while treatment in the presence of 6 percent carbon resulted in a removal of 99 percent of the iron and 22 percent of the titanium. The high percentage removal of iron in such a case as the latter example may be particularly advantageous where it is desired to secure a product, which is extremely free of iron, in a single operation.

It will be appreciated from an examination of Figure 1, that the carbon concentration may be so regulated that substantially all of the iron is removed, leaving the major portion of the titanium in the residue. The concentration of carbon used depends upon the amounts of iron and titanium in the ore and upon the desired purity of the residue. In general, it is preferred to introduce from one to twelve percent by weight of carbon calculated upon the weight of the ore being treated. Preferably, we maintain the carbon concentration within a range of approximately 2-9 percent of the weight of the ore.

The optimum amount of carbon required in order to secure maximum iron removal with minimum loss of titanium varies to some degree with the composition of the ore. Thus, for an ore containing 26 percent iron and 35 percent titanium, the optimum range of carbon concentration is 3.5-6 percent based upon the weight of the ore. With ores containing additional iron, the optimum carbon concentration is somewhat higher and with ores containing less iron, somewhat lower. While the process is adapted for treatment of various ores, it is preferred to treat titanium ores, containing 15 to 35 percent iron and 20-50 percent or more titanium, such as ilmenite, by this process. It will be apparent from the graph that there will be a highly effective removal of iron for a low titanium loss when the carbon concentration is at an optimum. Within the preferred range of temperature, with higher proportions of added carbon, there are similar slightly greater losses of titanium dioxide

with increase in carbon content; but at the same time, there is a somewhat greater effectiveness in removal of iron with a consequent lower iron content in the residual titanium dioxide.

The ore may be chlorinated in a coarse or finely ground state or in the form of briquettes or other suitable form, mixed with the required proportion of carbonaceous material such as charcoal, coke or the like. Preferably, the ore is ground to minus 100 mesh or finer and is intimately intermixed with finely divided carbon such as charcoal, petroleum coke, etc., preferably to such an extent as to prevent the existence of zones in the mixture wherein the carbon concentration is so high that a substantial amount of titanium tetrachloride may be driven off with the iron chlorides. We have found it desirable to briquette finely ground carbon-ore mixtures prior to chlorination. These briquettes may be bonded with a suitable binder such as molasses, tar, still residue derived from the distillation of mineral oils, asphalt, bitumen, sodium silicate or other convenient adhesive. Where the binder is carbonaceous, a corresponding reduction in the amount of carbon introduced into the mixture may be permissible. Care should be taken in forming the briquettes to insure sufficient porosity to permit permeation by the chlorine.

When chlorinating briquettes in accordance with our invention, it may be desirable to introduce a quantity of carbon in the form of coke, coal, etc., with the briquettes. Carbon so introduced does not appear to effect the amount of titanium volatilized during the chlorination to the same degree as the carbon in the briquettes since it is not in such intimate contact with the ore, and does not present the same amount of surface immediately adjacent the ore particles, but it burns in the presence of air, which may be introduced into the chlorination chamber, giving off heat. However, excess carbon mixed with the briquettes may compensate to some degree for a deficiency of carbon in the briquettes. In general, the temperature of treatment may be controlled and undue cooling of the reaction zone may be prevented by carbon introduced in this manner. In addition, carbon so introduced removes or decreases the concentration of air or oxygen which may enter the reaction zone through leakage and which would otherwise result in a decrease in the amount of iron removed.

In subjecting the ore to chlorination, we may use pure chlorine or we may chlorinate in the presence of a suitable diluent such as nitrogen, carbon dioxide, etc. If desired, reducing gases such as carbon monoxide may be introduced into the furnace to assist in the reaction.

The gases removed from the reaction chamber may contain quantities of chlorine, carbon monoxide, etc. In the event that it is desired to incorporate reducing gases in the chlorinating gas, this exhaust gas may be treated to remove suspended impurities and after removal of ferric chloride by condensation or other method, may be reintroduced into the reaction chamber with or without additional chlorine. In some cases, where the chlorination is carried out in more than one stage, the exhaust gases from one stage may be used as the chlorinating agent alone or with additional chlorine in earlier stages of the process. This not only serves as a means of conserving chlorine, but also may permit a very efficient preheating of the incoming ore.

If desired, the ore may be given a preliminary chlorination in the absence of reducing agents

prior to chlorination in the presence of carbon as heretofore described. Since such a chlorination may remove a portion of the iron initially present, the removal of the major portion of the iron by subsequent chlorination in the presence of the proper amount of carbon may be rendered less difficult.

Ferric chloride is volatilized and is removed with the exhaust gases. It may be precipitated by passing the gases through a suitably cooled condenser whereupon the iron chloride condenses as a solid product of reasonable purity. If desired, the ferric chloride may be precipitated by an electrostatic process or recovered as a solution by contacting the gases with water.

The chlorination may be carried out continuously, in batches or in any other convenient manner in suitable furnaces as, for example, induction or resistance type electrical furnaces, kilns, roasting ovens, etc.

It is preferred to operate the process continuously in suitable apparatus such as a shaft furnace. In order to start the process, the furnace may be preheated and when it has been heated to a desirable temperature, for example, above 500° C., an initial charge of ore may be introduced. This charge may consist of a mixture of lump carbon or coke and briquettes containing carbon and ore. Sufficient oxygen or air is introduced to ignite the carbon and to cause it to burn while chlorine is introduced in order to initiate the chlorination reaction. Further charges of briquettes and carbon may be introduced as the reaction proceeds. When the temperature exceeds 500° C. it is found that the chlorination reaction occurs with such rapidity and with sufficient evolution of heat that the temperature may be maintained without further introduction of air for combustion purposes. When the charge is brought up to temperature, partly or entirely by external heating, after such temperature is reached external heating may be discontinued.

In order to keep the process in continuous operation, it is preferred to introduce the ore, carbon, chlorine and oxygen, if necessary, at such a rate that the temperature is maintained above 500° C., preferably at 700–1150° C. Ordinarily, this may be done by regulating the rate of introduction of carbon-ore mixtures or briquettes in accordance with the periodic or continuous observation of the temperature in the reactor. Thus, if the temperature begins to decrease, the rate of introduction of the chlorine and the ore-carbon mixture may be increased while if the temperature increases, the rate of ore, carbon and chlorine introduction may be decreased. It will be understood that the carbon concentration in the ore-carbon mixtures or briquettes should not be in such excess that substantial amounts of titanium are lost. It will also be understood that the temperature may be regulated to some degree by the rate of withdrawal of the chlorinated residue. Thus, if required, a large amount of excess heat may be dissipated by rapid removal of the residue and the reactor cooled by the cool incoming ore.

If difficulty is encountered in maintaining the temperature by the heat of the chlorination reaction, carbon lumps may be added to the reaction zone with or without a charge of briquettes and air or oxygen introduced to burn sufficient carbon to raise the temperature to the desired value. Occasionally, the heat developed during the reaction is so great that the temperature of

the reaction zone approximates the sintering temperature of the ore. The reaction zone may be cooled, if desired, by introduction of a diluent gas such as nitrogen or carbon dioxide or by the methods hereinbefore referred to. Carbon dioxide appears to be particularly effective as a cooling gas in the reaction. Since substantially uniform results may be secured throughout the range of 700–1150° C., considerable latitude in temperature regulation is found to be permissible so long as the temperature remains within this range.

The following examples illustrate the invention as applied to the treatment of ilmenite ores. Other iron-titanium ores may be treated in similar manner.

Example I.—100 parts by weight of ilmenite ore containing 26 percent iron and 35 percent titanium was mixed with 4 parts by weight of carbon and 12 parts by weight of molasses and the mixture was made up into briquettes having an average size of $\frac{1}{2}$ inch in diameter and baked at 400° C. until volatile hydrocarbons were substantially removed. The total carbon content of the briquettes was 5.6 percent of the weight of the briquettes.

10 parts by weight of the briquettes were treated with 20 parts by weight of chlorine by heating the briquettes to a temperature of 980° C. and passing a stream of chlorine through the charge of briquettes. The temperature was maintained at 980° C. The residue contained 92.8 percent TiO_2 and 0.88 percent Fe_2O_3 . The removal of iron was thus 97 percent of the original iron content of the ore while the loss of titanium was only 2 percent.

Example II.—100 parts of ilmenite ore containing 26 percent Fe and 35 percent Ti was mixed with 6 parts of carbon and 12 parts molasses and the mixture was made up into briquettes having an average size of $\frac{1}{2}$ inch and baked at 400° C. to remove volatile hydrocarbons. The total carbon content of the briquettes was 7.2 percent of the weight of the briquettes.

10 parts by weight of the briquettes were treated with 20 parts by weight of chlorine by heating the briquettes to a temperature of 815° C. and passing a stream of chlorine through the charge of briquettes. The temperature was maintained at 815° C. The residue contained 90.0 percent TiO_2 and 0.71 percent Fe_2O_3 . The removal of iron was 98 percent of the original iron content of the ore, while the loss of titanium was only about 4 percent.

Example III.—A quantity of briquettes $\frac{1}{2}$ –1 $\frac{1}{2}$ inches in diameter were prepared from a mixture of 100 parts by weight of ore, $3\frac{1}{2}$ parts by weight of carbon and 12 parts by weight of molasses by baking at 400–600° C. until the volatile hydrocarbons were substantially removed. The total carbon content of the briquettes was about 5 percent of the weight of the briquettes.

A shaft furnace having an internal diameter of 6 $\frac{1}{2}$ inches was preheated by a coke fire within the shaft to 1100° C. A charge of 9 pounds of briquettes and 4 pounds of coke was introduced and an air blast through the shaft maintained for 5 minutes to insure ignition of the added coke. At this time, 10 pounds of briquettes were added and chlorine introduced into the shaft to initiate the chlorination reaction. The process was carried on continuously for many hours by introducing briquettes at a rate of 15–20 pounds per hour and chlorine at a rate of 40–50 liters per minute and withdrawing the treated residue

at a rate required to keep the ore in the furnace at constant level. The temperature remained at 850–1150° C. throughout the reaction. The product withdrawn from the bottom of the furnace contained 2.8–2.9 percent iron and 86.1 percent titanium dioxide. No external heat was required to maintain the reaction.

The ore after chlorination is found to have a high content of titanium dioxide in which a quantity (usually not more than 2–10 percent) of impurities such as iron, silica, alumina, etc., may be present. It may be used without further treatment for certain purposes. If desired, however, this product may be subjected to a second chlorination to remove titanium therefrom as titanium tetrachloride. This may be done in suitable manner, for example, by chlorinating in the presence of an excess of carbon as more fully discussed in our copending application, Serial No. 205,323 filed April 30, 1938.

In accordance with the process set forth in the above application, the residue may be chlorinated in the presence of a large excess of carbon and both iron and titanium volatilized as chlorides. These vapors may be simultaneously condensed whereby a suspension of solid ferric chloride in the liquid titanium is formed. The suspended ferric chloride may be removed by suitable methods such as by settling, and/or by filtration and the purified titanium tetrachloride recovered. The purified tetrachloride may be decomposed to form titanium dioxide, if desired.

Hydrogen chloride, phosgene or other gaseous chlorinating agents may be used in conjunction with chlorine in accordance with my invention.

Although this invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

We claim:

1. The process of removing iron from an iron-titanium ore which comprises chlorinating an intimate mixture of said ore and from 1 to 12 percent by weight of carbon, at a temperature above 500° C., the amount of carbon being sufficient to cause volatilization of the major portion of the iron without volatilizing the major portion of the titanium, whereby a residue which is largely titanium dioxide containing only a minor amount of iron is produced.

2. The process of removing iron from an iron-titanium ore which comprises chlorinating an intimate mixture of said ore and from 1 to 12 percent by weight of carbon, at a temperature of 700 to 1150° C., the amount of carbon being sufficient to cause volatilization of the major portion of the iron without volatilizing the major portion of the titanium, whereby a residue which is largely titanium dioxide containing only a minor amount of iron is produced.

3. The process of removing iron from an iron-

titanium ore which comprises chlorinating an intimate mixture of said ore and from 2 to 9 percent by weight of carbon, at a temperature above 500° C., the amount of carbon being sufficient to cause volatilization of the major portion of the iron without volatilizing the major portion of the titanium, whereby a residue which is largely titanium dioxide containing only a minor amount of iron is produced.

4. The process of removing iron from an iron-titanium ore which comprises chlorinating an intimate mixture of said ore and from 2 to 9 percent by weight of carbon, at a temperature of 700 to 1150° C., the amount of carbon being sufficient to cause volatilization of the major portion of the iron without volatilizing the major portion of the titanium, whereby a residue which is largely titanium dioxide containing only a minor amount of iron is produced.

5. The process of removing iron from ilmenite ore which comprises chlorinating an intimate mixture of said ore and 2 to 6 percent by weight of carbon at a temperature above 500° C., whereby a substantial amount of iron is volatilized and a residue is produced which is largely titanium dioxide containing less than 10 percent of the iron initially in the ore.

6. A continuous process of chlorinating ilmenite ore which comprises chlorinating a mixture of carbon and ore in a reaction zone, and introducing chlorine, carbon and ore into the reaction zone at such a rate that sufficient heat is evolved from the reaction to maintain a temperature of 700–1150° C. within at least a portion of the reaction zone without externally heating said zone.

7. A continuous process of chlorinating ilmenite ore which comprises chlorinating a mixture of carbon and ore in a reaction zone, and introducing chlorine, carbon and ore into the reaction zone at such a rate that sufficient heat is evolved from the reaction to maintain a temperature of 700–1150° C., within at least a portion of the reaction zone without externally heating said zone, the amount of carbon introduced being within 1 to 12 percent by weight of the ore and being regulated to cause volatilization of the major portion of the iron and to leave a residue which is largely titanium dioxide and which contains only a minor portion of iron.

8. The process of removing iron from iron-titanium ore containing upwards of 20 percent titanium which comprises chlorinating an intimate mixture of said ore and from 2 to 9 percent by weight of carbon at a temperature above 500° C., the amount of carbon being sufficient to cause volatilization of the major portion of the iron without volatilizing the major portion of the titanium, whereby a residue which is largely titanium dioxide containing only a minor amount of iron is produced.

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