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I. E. MUSKAT ET AL

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CHLORINATION OF TITANIUM BEARING MATERIALS

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2 Sheets-Sheet 1

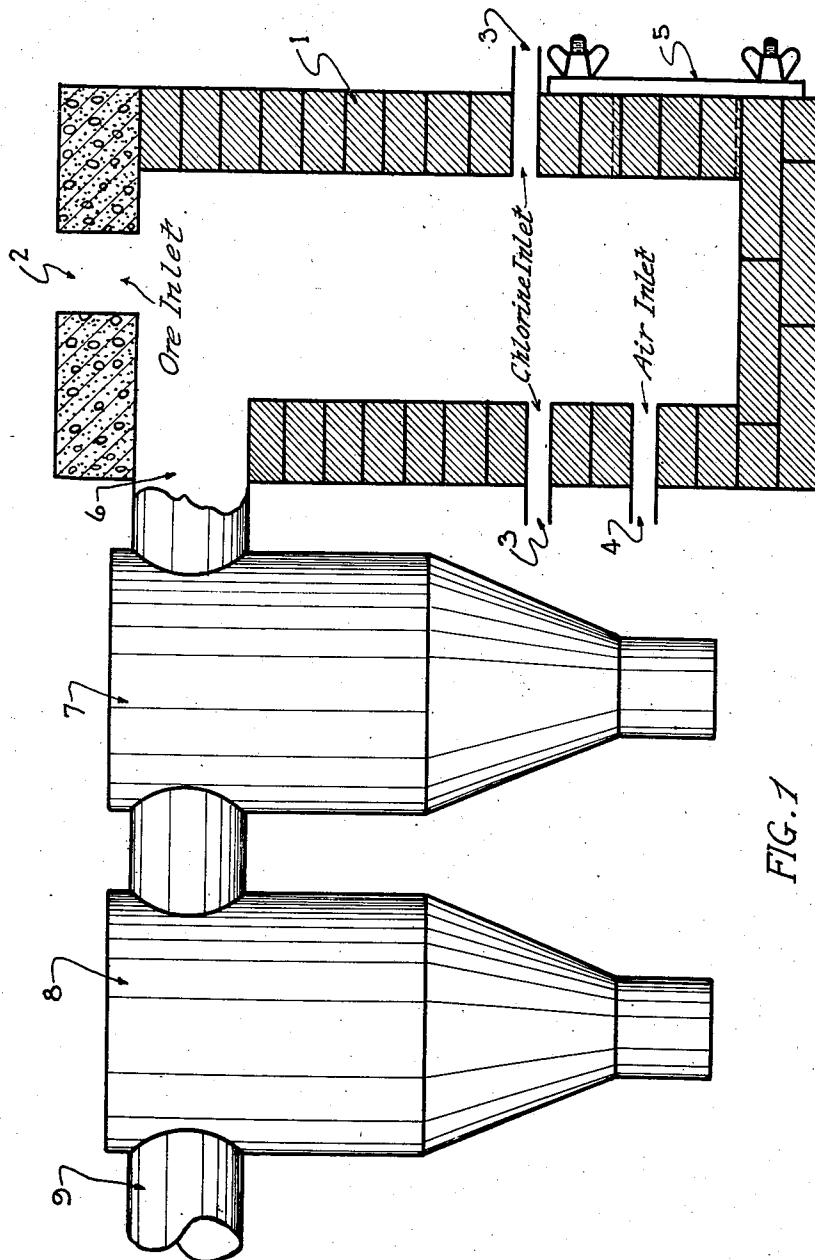


FIG. 1

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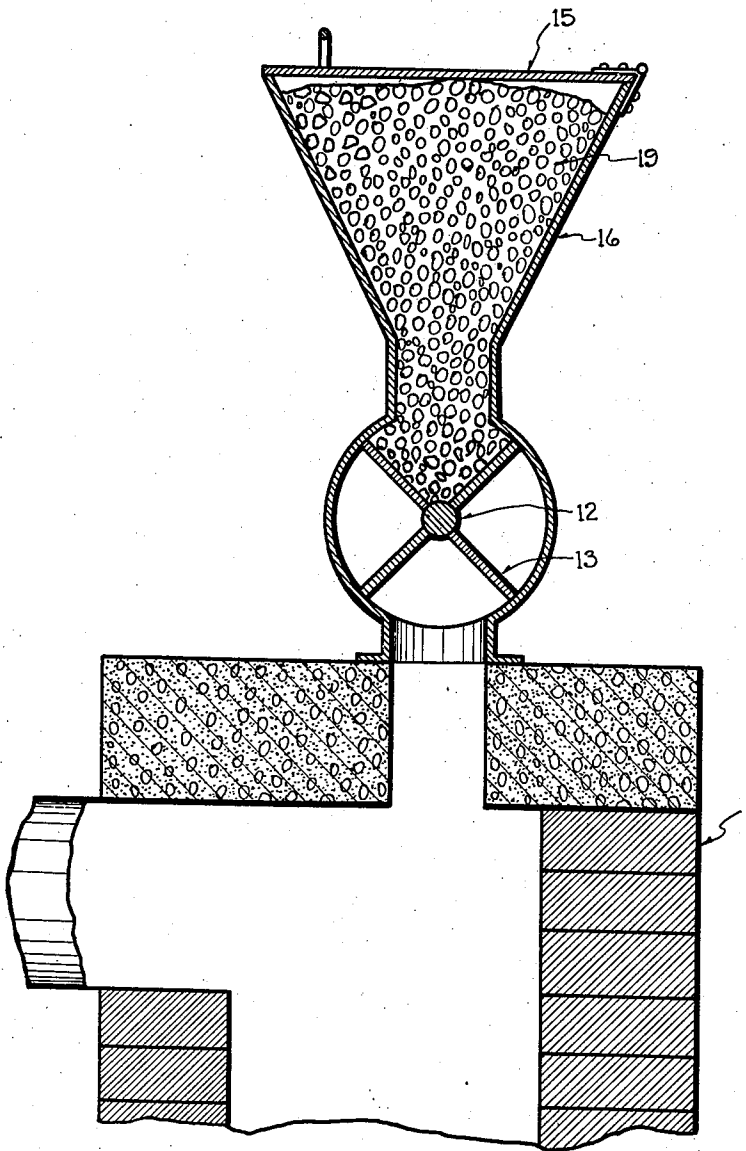


FIG. 2

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2,184,887

CHLORINATION OF TITANIUM BEARING MATERIALS

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Application June 30, 1939, Serial No. 232,198

15 Claims. (Cl. 75-112)

This invention relates to the chlorination of titanium bearing materials and is particularly adapted to the chlorination of materials containing titanium oxides such as ilmenite ore and to the recovery of values therefrom.

It has been found that in order to secure satisfactory chlorination of such materials it is necessary to chlorinate at elevated temperatures and prior to the present invention, it has been considered essential to conduct the chlorination in an externally heated receptacle such as a retort. This has required the use of receptacles which are made of materials of high conductivity and in general, such materials are attacked rapidly by chlorine at the temperature of operation.

In addition, the chlorination of these ores has generally resulted in the plugging of the apparatus with ferric chloride within a very short time after the process has been initiated, thus preventing continuous operation. For these reasons, no process of chlorinating titanium ores to produce titanium tetrachloride has achieved commercial success.

In accordance with our invention, we have found that the chlorination may be conducted without recourse to an externally heated reactor and that plugging may be substantially eliminated. The process is adapted to the treatment of titanium bearing materials containing from 20 to 50 per cent or more of titanium and generally above 10 per cent and up to 50 per cent of iron and is particularly adapted to the treatment of titanium bearing ores such as ilmenite which contain 20 to 50 per cent of titanium and 10 to 40 per cent of iron. Other ores such as titanomagnetite or titanium bearing residues such as are secured in accordance with the process described in our copending application Serial No. 205,323, filed April 30, 1938, also may be chlorinated. The chlorination is conducted in the presence of the required amount of a reducing agent such as carbon in a suitable furnace with the consequent production of vapors of iron and titanium tetrachloride. These vapors may be condensed and the chlorides therein separated by suitable means. We have found that if the chlorination is conducted at a temperature not less than 600° C. and preferably above 700° C., the reaction proceeds with such rapidity that the heat evolved by the reaction is sufficient to maintain reaction temperature without externally heating the reactor. Thus, by regulating the rate of introduction of ore, carbon and chlorine into the reactor, it is possible to maintain the temperature therein. This is not possible when the

chlorination temperature is below 600° C. In order to achieve optimum efficiency and yield, the temperature should be maintained above 700° C., maximum efficiency being secured at 850-1250° C. Thus, when an ore such as ilmenite is chlorinated at a temperature of about 700° C. or above, the temperature of reaction may be maintained through careful periodical observation of temperature and regulation of the rate of introduction of chlorine, ore and carbon. In such a case it is found possible to secure a good utilization of the chlorine introduced and to secure chlorination of the major portion of the ore without difficulty. When the temperature is maintained at 850-1250° C. maintenance of temperature within the reactor is considerably easier and less adjustment of the rate of addition of ore, carbon and chlorine is required. In addition, the chlorine utilization under such conditions generally exceeds 90 per cent and in excess of 80 per cent of the ore is generally chlorinated.

In the treatment of ores such as ilmenite, it is found that the required concentration of reducing agent is rather critical. In general, carbon concentrations below 15 per cent by weight of the ore are insufficient to insure complete chlorination of the iron and titanium components. On the other hand, excess carbon concentrations are found to be objectionable since the presence of the excess makes temperature maintenance difficult. For most purposes, the carbon concentration should be maintained at 15-35 per cent by weight of the ore. We have found that within limits the amount of titanium volatilized is proportional to the amount of carbon present. Thus, when an ilmenite ore containing 35.2 per cent of titanium and 25.8 per cent of iron is mixed with 2 to 6 per cent of carbon and chlorinated at high temperatures, for example, above 850° C., substantially all of the iron is volatilized as iron chloride leaving the titanium in the form of an oxide in the residue. As the carbon concentration is increased, more and more titanium may be volatilized as the tetrachloride by chlorination and when the carbon concentration is 15 to 35 per cent of the ore, in excess of 80 per cent of the ore is completely chlorinated. Further increases in carbon concentration do not appear to increase the efficiency of the reaction but on the contrary exert a quenching effect upon the reaction, thus making temperature maintenance very difficult. This may be compensated for to a degree by introduction of air or oxygen with the chlorine into the furnace in order to burn

the excess carbon with consequent evolution of heat.

The vapors of iron chloride and titanium tetrachloride thus formed may be condensed in any convenient manner. If desired, the two chlorides may be fractionally condensed whereby quantities of both chlorides may be secured. In many cases, however, it is difficult to secure satisfactory separation of the iron chloride in this manner. Consequently, the iron chloride often distributes itself throughout the condenser system, plugging the system to such an extent that it must be cleaned at frequent intervals. In order to avoid this plugging, it is often advisable to condense the major portion of the iron chloride shortly after it is withdrawn from the furnace. To insure the removal of iron chloride to such an extent that the possibility of plugging during subsequent condensation processes is minimized, it is found desirable to condense out all or a portion, generally not less than about 15-30 per cent of the titanium tetrachloride together with the iron chloride. Any residual titanium tetrachloride vapor may then be condensed without fear of plugging the condenser system.

The invention will be more fully understood by reference to the accompanying drawings in which Fig. 1 is a diagrammatic partially in section view of an apparatus which is suitable for use in the operation of the present invention and Fig. 2 is a diagrammatic sectional view of a device which may be used to feed the ore into the furnace.

Fig. 1 diagrammatically illustrates a suitable apparatus for conducting the process in accordance with our invention. The apparatus comprises a suitable shaft furnace 1, which may be constructed from firebrick or other resistant refractory material, and which is provided with chlorine tuyères 3, and one or more oxygen tuyères 4, and is connected to a series of condensers 7 and 8. In the ordinary operation of the furnace a charge of coke or other carbonaceous material may be introduced into the furnace, a blast of oxygen or air introduced through the tuyères 4, and the coke ignited. When the temperature has reached a suitable value, for example, 850° C., a charge of briquettes of ore and carbon may be introduced through furnace inlet 2, which is then closed by a suitable cover (not shown). At this time introduction of oxygen or air may be discontinued and chlorine is introduced into the furnace through tuyères 3. The chlorine flow rate is adjusted in accordance with the amount of ore introduced so that the amount of chlorine introduced is sufficient for complete chlorination. Additions of ore may be either continuous or intermittent. The base of the furnace is provided with a suitable door or other closure 5, at which ash and unchlorinated ore may be withdrawn continuously or intermittently. The iron and titanium chlorides which volatilize are withdrawn through outlet pipe 6, and may be led to condensers 7 and 8, where they may be condensed by convenient methods. The exhaust gases are withdrawn through conduit 9.

In the event that plugging is encountered during condensation, it may be desirable to condense most of the iron chloride shortly after it is removed from the furnace whereby only minor quantities of ferric chloride condense in other portions of the system. Such minor portions do not tend to cause plugging since they

may be removed by washing with liquid titanium tetrachloride. In order to secure a removal of substantially all or at least in excess of 85 per cent of the ferric chloride, a large portion generally in excess of 15-30 per cent of the titanium tetrachloride is condensed with the iron chloride. It is found that when a fractional condensation of iron chloride is attempted a large portion of the iron chloride remains dispersed in the uncondensed gases in the form of a finely divided smoke or solid suspension. When a substantial proportion of titanium tetrachloride is condensed with the ferric chloride, however, the condensed liquid tetrachloride bathes the gases and assists separation of the solid ferric chloride therefrom. The mixture of chlorides so condensed may then be heated to recover the titanium tetrachloride. In order to improve the separation of iron and titanium chlorides, it is desirable to heat the condensed mixture in the presence of a gaseous diluent. The gaseous mixture which remains after condensation of iron chloride and part of the titanium tetrachloride is found to be particularly suitable for a diluent since it is substantially free from oxygen or other agents which would promote decomposition of the chlorides.

Fig. 2 diagrammatically illustrates a suitable apparatus which may be used to feed the ore into the furnace in a continuous manner. In accordance with this modification a suitable hopper 16, is provided mounted upon furnace 1, adjacent the ore inlet thereof. The hopper is provided with a suitable cover 15, and is provided at the hopper base with a conventional star feeder device comprising blades 13, mounted upon the rotatable shaft 12. In the operation of this device a charge of briquettes or finely divided ore 19, is introduced into the hopper. By rotation of shaft 12, blades 13 sweep portions of the ore from the hopper permitting them to fall into the furnace in a continuous manner. It is to be understood, however, that the present invention is not limited to the use of the particular feed mechanisms herein illustrated and that various other feed mechanisms such as worm gear feeds, etc., may be used for the same purpose.

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 amount of carbonaceous material such as charcoal, coke or the like. If desired, the ore may be ground to minus 100 mesh or finer, and intimately intermixed with finely divided carbon such as peat, petroleum or coal, coke, charcoal, etc., the degree of intermixing being that required to obtain a composition which is approximately homogeneous.

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 a distillation of mineral oils, asphalt, bitumen, sodium silicate or other convenient adhesives. 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 penetration by the chlorine. The briquettes may be preheated before introduction into the furnace or they may be introduced cold. In general, it is desirable to preliminarily bake the briquettes in order to eliminate hydrocarbons which may volatilize dur-

ing the chlorination. If desired, the baked briquettes may be discharged into the furnace from the baking oven and while they are hot.

In order to start the process the furnace may be preheated and when it has been heated to a desirable temperature above 600° C., an initial charge of ore may be introduced. The furnace may be preheated by any suitable method such as by introducing coke, peat or other carbonaceous material into the furnace and sufficient air or oxygen to ignite and burn the carbon. A mixture of ore and carbon may be introduced upon the burning carbon and chlorine is introduced to initiate the chlorination reaction. Further charges of ore and carbon may be introduced as the reaction proceeds. When the temperature exceeds 600° 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 or oxygen for combustion purposes.

As an alternative method of initiating the reaction, the briquettes or charge of ore and carbon may be heated prior to introduction into the furnace to a temperature above 600° C., and preferably 850–1250° C., and chlorine introduced into the heated charge. In addition, the furnace may be preheated by other methods such as by heating the interior thereof by introducing and burning natural gas or similar gas into the furnace to preheat the furnace to a temperature above 600° C.

In order to keep the process in continuous operation, it is preferred to introduce to ore, carbon and chlorine at such a rate that the temperature is maintained above 600° C., preferably at 850–1250° C. Ordinarily, this may be done by regulating the rate of introduction of chlorine and carbon-ore mixtures or briquettes in accordance with 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 of 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 also be understood that the temperature may be regulated to some degree by the rate of withdrawal of the chlorinated residue. Thus, a large amount of heat may be dissipated by rapid removal of the residue and the reactor cooled by the incoming cool ore.

Occasionally, the heat developed during the reaction is so great the temperature of the reaction zone approximates the sintering temperature of the ore. The reaction may be cooled, if desired, by introduction of a diluent gas such as nitrogen or carbon dioxide or by use of chlorine diluted with these or other diluents. 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 850–1250° C., considerable latitude in temperature regulation may be permissible so long as the temperature remains within this range. As previously noted, however, operation is considerably more efficient when the temperature is kept at 850–1250° C. The process may be continued for an extended length of time without application of external heat to the furnace. Accordingly, it is possible to construct the furnace of materials which are highly resistant to the corrosive action of chlorine at the temperature of operation. Since it is unnecessary to apply

external heat to the furnace, the use of heat conductive furnace construction materials is unnecessary. In fact such materials are in general undesirable since it is usually preferred to construct the furnace of heat insulating materials in order to prevent substantial loss of heat and consequent cooling of the reaction. Fire brick has been found to exhibit satisfactory resistance to the attack of chlorine and to possess suitable heat insulating qualities.

In order to assist the volatilization of iron and titanium chlorides and thus promote the rate of reaction within the furnace and to prevent plugging therein, it is often desired to conduct the chlorination in the presence of at least 4 percent by volume of oxygen based upon the weight of chlorinating gas. This oxygen not only assists the removal of the titanium tetrachloride but also prevents formation of high melting point chlorides such as magnesium chloride. An excess concentration of air or oxygen is undesirable since it results in an undesirable dilution of the chlorine and consequent quenching of the reaction. In general, chlorine should constitute at least 30 percent by volume of gases entering the furnace.

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

Example I.—A quantity of briquettes $\frac{1}{4}$ to $\frac{3}{4}$ inch in diameter were prepared from a mixture of 100 parts by weight of ilmenite ore, 26 parts by weight of carbon, and 14 parts by weight of molasses by baking at 600° C. until the volatile hydrocarbons were substantially removed. The carbon content of the briquettes was about 20 percent of the weight of the briquettes.

A shaft furnace, having an internal diameter of 4 inches, was preheated by a coke fire within the shaft to 1000° C. A charge of 5 pounds of briquettes and 3 pounds of coke was introduced and an air blast through the shaft maintained for 3 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. Chlorine was introduced into the shaft at a rate of 50–60 liters per minute, while briquettes were added at the rate of 15 pounds per hour. For a period of over 24 hours, the temperature of the reaction mass was very readily maintained at 940° C. to over 1100° C. An ash containing 15% TiO_2 and 5% Fe was withdrawn from the furnace. Since the quantity of this ash approximated 10% of the weight of the briquettes added, 96% of the titanium content of the ore was volatilized as titanium tetrachloride and 98% of the iron was volatilized as iron chloride.

Example II.—Using a furnace having an internal diameter of 15 inches which was preheated to a temperature of 1000° C., briquettes prepared from a mixture corresponding to 100 parts ore to 23 parts C to 14 parts molasses, were introduced at a rate of 120 pounds per hour and chlorine at 2.0 to 2.5 pounds per minute. The temperature remained at 850–1000° C. throughout the run without externally heating the furnace. The vapors were withdrawn from the furnace and cooled to 40° C. whereupon 85 percent of the ferric chloride and 25 percent of the titanium tetrachloride were simultaneously condensed. The condensed chlorides were transferred to another portion of the condenser where the titanium tetrachloride was revolatilized by

heating while passing the exhaust gases of the furnace over the condensed chlorides. The process was carried on continuously for many hours by introducing briquettes at a rate of 120 pounds per hour, and chlorine at a rate of 2.0 to 2.5 pounds per minute. The treated residue was withdrawn at a rate required to keep the ore in the furnace at a constant level.

Hydrogen chloride, phosgene, carbon tetrachloride or other gaseous chlorinating agents may be used in conjunction with chlorine in accordance with our invention. While the invention has been described with particular reference to the chlorination of oxide ores such as ilmenite it may also be applied to metallic residues such as ferrotitanium.

Although the present 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. This application is a continuation-in-part of our copending applications Serial Nos. 205,322, 205,323 and 206,219, filed April 30, 1938.

We claim:

1. A continuous process of chlorinating a titanium oxide bearing material which contains 20 to 50 percent of titanium and about 10 to 50 percent of iron which comprises chlorinating a mixture of said material and about 15 to 35 percent by weight of carbon in the reaction zone of a reactor and introducing chlorine, carbon and said material therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature not less than 600° C., within at least a portion of the zone without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

2. A continuous process of chlorinating a titanium oxide bearing material which contains about 20 to 50 percent of titanium and about 10 to 50 percent of iron which comprises chlorinating a mixture of said material and about 15 to 35 percent by weight of carbon in the reaction zone of a reactor and introducing chlorine, carbon and said material therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature above 700° C. within at least a portion of the zone without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

3. A continuous process of chlorinating a titanium oxide bearing material, which comprises chlorinating a mixture of said material and about 15 to 35 percent by weight of carbon in the reaction zone of a reactor and introducing chlorine, carbon and said material therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature of about 850-1250° C. within at least a portion of the zone, without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

4. A method of initiating and conducting the chlorination of ilmenite ore which contains about 20 to 50 percent of titanium and about 10 to 50 percent of iron which comprises introducing a combustible carbonaceous material into the reaction zone of a reactor, igniting said carbonaceous material and introducing oxygen into said zone to support combustion of the said carbonaceous material and to heat the interior of the reactor to a temperature above 600° C., introducing a mixture of the ore and about 15 to 35

percent by weight of carbon into the reactor, introducing chlorine to initiate the chlorination and continuing the addition of the ore, carbon and chlorine at a rate such that the heat evolved by the chlorination reaction is developed with sufficient rapidity to maintain the temperature within at least a portion of the said zone above 600° C.

5. A method of initiating and conducting the chlorination of a titanium bearing material which contains about 20 to 50 percent of titanium and about 10 to 50 percent of iron which comprises introducing a combustible carbonaceous material into the reaction zone of a reactor, igniting the said carbonaceous material and introducing oxygen into said zone to support combustion of said carbonaceous material and to heat the interior of the reactor to a temperature above 600° C., introducing a mixture of titanium bearing material and carbon into the reactor, introducing chlorine to initiate the chlorination and continuing the addition of titanium bearing material, carbon and chlorine at a rate such that the heat evolved by the chlorination reaction is developed with sufficient rapidity to maintain the temperature within at least a portion of said zone above 600° C. the amount of carbon introduced being sufficient to insure conversion of the major portion of the titanium to titanium tetrachloride.

6. A continuous process of chlorinating ilmenite ore containing about 20 to 50 percent of titanium and about 10 to 40 percent of iron which comprises chlorinating a mixture of said material and sufficient carbon to cause formation of iron chloride and a major quantity of titanium tetrachloride in the reaction zone of a reactor and introducing chlorine, carbon and ore therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature above 600° C. within at least a portion of the zone without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

7. A continuous process of chlorinating ilmenite ore containing about 20 to 50 percent of titanium and about 10 to 40 percent of iron which comprises chlorinating a mixture of said material and sufficient carbon to cause formation of iron chloride and a major quantity of titanium tetrachloride in the reaction zone of a reactor and introducing chlorine, carbon and ore therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature of about 850-1250° C., within at least a portion of the zone without externally heating the said zone, whereby iron and titanium chlorides are formed and volatilized.

8. The process of initiating and conducting the chlorination of a titanium bearing material containing about 20 to 50 percent of titanium and about 10 to 50 percent of iron which comprises preheating the reaction zone within a reactor above about 700° C., introducing a charge of titanium bearing material which has been heated to a temperature above about 700° C., into the reaction zone, introducing chlorine to initiate the reaction and continuing the addition of said material, carbon and chlorine at a rate such that the heat evolved by the chlorination is developed with sufficient rapidity to maintain the temperature within at least a portion of the reaction zone above 700° C., without externally heating the reaction zone, the amount of carbon introduced being sufficient to insure conversion

of the major portion of the titanium to titanium tetrachloride.

9. The process of initiating and conducting the chlorination of ilmenite ore containing about 20 to 50 percent of titanium and about 10 to 40 percent of iron which comprises preheating the reaction zone within a reactor above about 850° C., introducing a charge of said titanium bearing material and carbon into the reaction zone, introducing chlorine to initiate the reaction and continuing the addition of said material, carbon and chlorine at a rate such that the heat evolved by the chlorination is developed with sufficient rapidity to maintain the temperature within at least a portion of the reaction zone above 850° C., without externally heating the reaction zone the amount of carbon introduced being sufficient to insure conversion of the major portion of the titanium to titanium tetrachloride.

10. A process of chlorinating a titanium bearing material containing at least about 20 to 50 percent of titanium which comprises subjecting a mixture of said material to the action of a controlled amount of chlorine and an independently controlled amount of oxygen at a temperature not less than about 600° C., the amount of carbon present being sufficient to insure the conversion of the major portion of the titanium to titanium tetrachloride.

11. A process of chlorinating a titanium bearing material containing at least about 20 to 50 percent of titanium which comprises chlorinating a mixture of said material and a sufficient reducing agent sufficient to insure conversion of a major portion of the titanium to titanium tetrachloride in the reaction zone of a reactor and introducing chlorine, carbon and said material therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature of about 850-1250° C. within at least a portion of the zone, without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

12. A process of chlorinating a titanium bearing material containing at least about 20 to 50 percent of titanium which comprises chlorinating a mixture of said material and a sufficient reducing agent sufficient to insure conversion of a major portion of the titanium to titanium tetrachloride in the reaction zone of a reactor and introducing chlorine, carbon and said material therein at such a rate that sufficient heat is

evolved from the reaction to maintain the temperature above 700° C., within at least a portion of the zone, without externally heating the said zone, whereby iron and titanium chlorides are formed and volatilized.

13. A continuous process of chlorinating an ilmenite ore which contains 20 to 50 percent of titanium and about 10 to 40 percent of iron which comprises chlorinating a mixture of said ore and about 15 to 35 percent by weight of carbon in the reaction zone of a reactor and introducing chlorine, carbon and said ore therein at such a rate that sufficient heat is evolved from the reaction to maintain the temperature not less than 600° C., within at least a portion of the zone without externally heating said zone, whereby iron and titanium chlorides are formed and volatilized.

14. A continuous process of chlorinating ilmenite ore containing about 20 to 50 percent of titanium and 10 to 40 percent of iron which comprises chlorinating a mixture of said material and sufficient carbon to cause formation of iron chloride and a major quantity of titanium tetrachloride in the reaction zone of a reactor, briquetting the ore and carbon, baking the briquettes and introducing chlorine and the baked briquettes containing ore and carbon at such a rate that sufficient heat is evolved from the reaction to maintain the temperature above 600° C. within at least a portion of the zone without externally heating the reactor, whereby iron and titanium chloride are formed and volatilized.

15. A continuous process of chlorinating ilmenite ore containing at least 20 percent titanium which comprises introducing a mixture of ore and sufficient carbon to cause formation of iron chloride and a major quantity of titanium tetrachloride into the upper portion of a shaft furnace, introducing chlorine in a lower portion of said furnace maintaining the temperature above 600° C. whereby the ore is chlorinated and continuing the introduce of ore chlorine and carbon at such a rate that sufficient heat is evolved from the reaction to maintain the temperature above 600° C. within at least a portion of the reaction zone of the furnace without externally heating the furnace, whereby iron and titanium chloride are formed and volatilized.

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