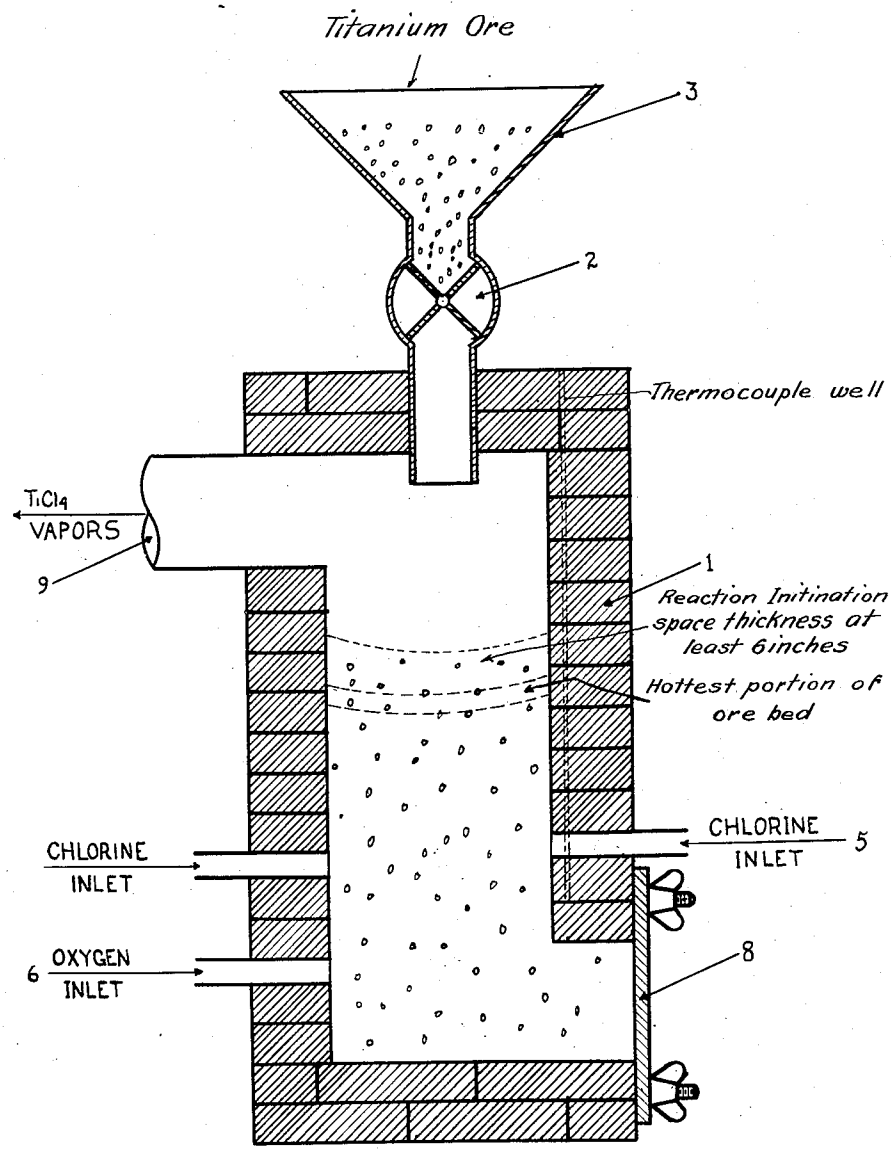
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CHLORINATION OF TITANIUM BEARING MATERIALS

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CHLORINATION OF TITANIUM BEARING MATERIALS

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

In our prior applications Serial No. 206,219, filed April 30, 1938, and Serial No. 282,198, filed June 30, 1939, we have described and claimed a process wherein titanium bearing materials are chlorinated in a furnace under conditions such that the heat generated during the reaction is sufficient to maintain the temperature at a suitable value without externally heating the furnace. In operating this process it has been observed that occasionally the chlorine utilization is objectionably low. In accordance with the present invention, it is found that by chlorinating a relatively deep bed of ore the chlorine utilization may be raised to such an extent that substantially complete chlorine utilization is secured. In operating with such a deep ore bed, however, it is observed that the upper portion thereof often is relatively cool. Since, in practice, the vaporized metal chlorides are withdrawn from an upper portion of the ore bed, condensation of a substantial portion of vaporized iron chloride upon the cool portion of the ore bed often occurs, thus causing plugging or bridging within the furnace. This is particularly true when cold ore is introduced upon a relatively deep ore bed. In addition, the cold ore cools the surface of the ore bed to such a degree that the chlorine utilization is appreciably lowered.

We have found that the chlorination process may be substantially improved in efficiency by maintaining the temperature of the upper portion of the ore bed above the temperature at which ferric chloride condenses, preferably about 200° C. This may be accomplished, for example, by preliminarily heating the ore prior to its introduction into the reaction zone of the chlorinating furnace. By this means plugging within the furnace due to condensation of iron chloride is substantially eliminated. In addition, the chlorination reaction proceeds with greater vigor and the capacity of the furnace is greatly increased.

The process is adapted to the treatment of titanium bearing materials containing from 20 to 50 percent or more of titanium and generally above 10 percent and up to 50 percent of iron and is particularly adapted to the treatment of ferro titanium or titanium bearing ores such as ilmenite which contain 20 to 50 percent of titanium and 10 to 40 percent of iron. Other ores such as titanomagnetite or titanium bearing residues such as are secured in accordance with our 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 chloride 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 95 percent and in excess of 85 percent 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 percent 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 percent by weight of the ore. We have found that within limits the amount of titanium volatilized is pro-

portional to the amount of carbon present. Thus, when an ilmenite ore containing 35.2 percent of titanium and 25.8 percent of iron is mixed with 2 to 6 percent 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 percent of the ore, in excess of 80 percent 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 the 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 ore is preferably heated to a temperature above 200° C. prior to introduction into the reaction. The rate of ore introduction is regulated in accordance with the rate of chlorination and in general, is regulated to secure a bed having a depth of at least about 6 inches and preferably in excess of one foot, measured from the hottest portion of the ore bed to the top of the bed.

Generally it is desirable to briquette the ore and carbon mixture 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 tar, etc. These briquettes are usually baked to eliminate volatile hydrocarbons at a temperature of 300 to 600° C. and if desired, the briquettes may be discharged directly into the furnace as they are removed hot from the baking oven, thus eliminating the necessity of further preheating.

The accompanying drawing diagrammatically illustrates a sectional view of a suitable apparatus for conducting the process in accordance with our invention. The apparatus comprises a suitable shaft furnace 1, which may be constructed of firebrick or other refractory and which is provided with chlorine tuyères 5, oxygen tuyères 6, an ore feed device 2, and an outlet 9, for evolved vapors. In the normal operation of this device, a charge of coal or other carbonaceous material may be introduced into the furnace, oxygen introduced through tuyères 6, and coke is ignited. When the temperature has reached a suitable value, for example, 850° C., a charge of briquettes of ore and carbon may be introduced and chlorine introduced through tuyères 5. Hopper 3, is filled with preheated ore and carbon generally in the form of briquettes which are discharged into the furnace at a controlled rate through star feeding device 2. The base of the furnace is provided with a suitable door, or other closure 8, at which ash and unchlorinated ore may be withdrawn continuously or intermittently. The iron and titanium chlorides which volatilize are withdrawn through outlet 9, and are condensed by suitable means.

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.

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 the 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 mixtures 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 ore.

By preheating the ore prior to its introduction, it is possible to operate with a relatively deep ore bed, thus permitting more intimate contact of the chlorine and the ore and effecting a more efficient utilization of chlorine. In general, it is desirable to regulate the rate of ore addition so that the hottest portion of the reaction zone is a substantial distance below the top of the ore bed and for most cases the hottest zone should be at least about 6 inches and preferably not less than one foot, below the top of the ore bed. In this manner, it is possible to secure substantially complete chlorine utilization. The depth of the bed may be ascertained by means of a pyrometer and by providing the furnace with a suitable well for introduction of thermocouple wires. Since the top of the ore bed will be substantially cooler iron chloride sometimes condenses when the depth of the bed is excessive. Preheating of the ore above the condensation temperature of ferric chloride eliminates this condensation tendency.

Occasionally the heat developed during the re-

action 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 ¼ to ¾ inches 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 briquette.

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 maintained for 3 minutes through the shaft to insure ignition of the added coke. At this time, 10 pounds of briquettes were added and chlorine introduced into the shaft at a rate of 75–80 liters per minute, while briquettes preheated to 400–600 C. were added at the rate of 20 pounds per hour and the depth of ore bed was maintained at 3 feet measured from the hottest portion of the reaction to the top of the bed. 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 8% 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 preheated to 600° C. and introduced at a rate of 175 pounds per hour and chlorine introduced at 3.0 to 3.5 pounds per minute, the depth of the ore bed being maintained at 24 inches. The temperature remained at 850–1000° C. throughout the run without externally heating the furnace. The vapors were withdrawn from the furnace and condensed. 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 ore 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.

We claim:

1. A continuous process of chlorinating iron titanium ore containing at least about 20 percent of titanium which comprises forming a pervious bed containing ore and carbon, passing chlorine through said bed, maintaining the temperature above about 600° C., withdrawing vaporized chlorides from the surface of said bed, introducing a further quantity of fresh ore and carbon and regulating the rate of introduction of ore to insure a bed of ore at least about 6 inches deep measured from the hottest portion of the ore bed to the top of said bed.

2. A continuous process of chlorinating an iron titanium ore containing at least about 20 percent of titanium which comprises forming a pervious bed containing ore and carbon, passing chlorine through said bed, maintaining the temperature above about 600° C., withdrawing vaporized chlorides from the surface of said bed, introducing a further quantity of fresh ore and carbon and regulating the rate of introduction of ore to insure a bed of ore at least about 12 inches deep measured from the hottest portion of the ore bed to the top of said bed.

3. A continuous process of chlorinating an iron titanium ore containing at least about 20 percent of titanium which comprises forming a pervious bed containing ore and carbon, passing chlorine through said bed, maintaining the temperature above about 600° C., withdrawing vaporized chlorides from the surface of said bed, introducing a further quantity of fresh ore and carbon and regulating the rate of introduction of ore to insure a bed of ore at least about 12 inches deep measured from the hottest portion of the ore bed to the top of said bed, and maintaining the temperature of the ore adjacent the surface of the ore bed at a temperature above about 300° C.

4. A continuous process of chlorinating a ti-

tanium bearing material containing at least about 20 percent of titanium which comprises forming a pervious bed containing said material and carbon, passing chlorine through said bed, maintaining the temperature above about 600° C., withdrawing vaporized chlorides from the surface of said bed, introducing a further quantity of fresh titanium bearing material and carbon and regulating the rate of introduction of titanium bearing material to insure a bed of titanium bearing material at least about 12 inches deep measured from the hottest portion of the bed to the top of said bed, and maintaining the temperature adjacent the surface of the bed at a temperature above about 300° C.

5. A continuous process of chlorinating a titanium bearing material containing at least about 20 percent of titanium which comprises chlorinating a pervious bed of said material and carbon within a reactor at a temperature above 600° C., introducing a further quantity of said material and carbon upon the upper portion of the bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of the bed and maintaining the temperature of said upper portion sufficiently high to prevent substantial condensation of iron chloride in said upper portion.

6. A continuous process of chlorinating ilmenite ore containing at least about 20 percent of titanium which comprises chlorinating a pervious bed of said ore and carbon whithin a reactor at a temperature above 600° C., introducing a further quantity of said ore and carbon upon the upper portion of the bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of the bed and maintaining the temperature of said upper portion sufficiently high to prevent substantial condensation of iron chloride in said upper portion.

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, and preheating a quantity of the ore introduced into the reactor.

8. 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, and preheating a quantity of the ore introduced into the reactor.

9. 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 reaction mixture of said ore and sufficient carbon in a column to cause volatilization of iron and titanium chlorides, introducing ore into an upper portion of said column and introducing chlorine into a lower portion of the column and introducing ore, chlorine and carbon at such a rate that sufficient heat is evolved from the reactor to maintain the temperature above 600° C. within a portion of the shaft without externally heating the column and preheating ore introduced to a temperature above 300° C., whereby cooling of the upper portion of the reaction mixture is substantially minimized.

10. A continuous process of chlorinating titanium bearing material containing at least 20 percent titanium which comprises chlorinating a reaction mixture of said material and sufficient carbon in a column to cause volatilization of titanium chlorides, introducing material into an upper portion of said column and introducing chlorine into a lower portion of the column and introducing material, chlorine and carbon at such a rate that sufficient heat is evolved from the reaction to maintain the temperature above 700° C. within a portion of the shaft without externally heating the column and preheating material introduced to a temperature above 300° C., whereby cooling of the upper portion of the reaction mixture is substantially minimized.

11. A continuous process of chlorinating ilmenite ore which comprises chlorinating a pervious bed of said ore and carbon within a reactor at a temperature above 700° C., introducing ore and carbon upon the upper portion of said bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of said bed and maintaining the temperature of the ore adjacent the upper portion of said bed sufficiently high to prevent substantial condensation of iron chloride in said upper portion.

12. A continuous process of chlorinating ilmenite ore which comprises chlorinating a pervious bed of said ore and carbon within a reactor at a temperature above 700° C., introducing ore and carbon upon the upper portion of said bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of said bed and maintaining the temperature of the ore adjacent the upper portion of said bed above 300° C.

13. A continuous process of chlorinating ilmenite ore which comprises chlorinating a pervious bed of said ore and carbon within a reactor at a temperature above 700° C., introducing ore and carbon upon the upper portion of said bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of said bed and maintaining the temperature of the ore adjacent the upper portion of said bed sufficiently high to prevent substantial condensation of iron chloride in said upper portion by preheating incoming ore.

14. A continuous process of chlorinating ilmenite ore which comprises chlorinating a pervious bed of said ore and carbon within a reactor at a temperature above 700° C., introducing ore and carbon upon the upper portion of said bed to insure the presence of a layer of material of substantial thickness measured from the hottest portion of the bed to the top of the zone of chlorination and chlorine into a lower portion of said bed and maintaining the temperature of the

ore adjacent the upper portion of said bed above 300° C., by preheating incoming ore.

15. A continuous process of chlorinating ilmenite ore which comprises chlorinating a pervious bed of said ore and carbon within a reactor at a temperature above 700° C., introducing ore and carbon upon the upper portion of said bed and chlorine into a lower portion of said bed, at such a rate that sufficient heat is evolved from the chlorination to maintain the temperature above 700° C., without externally heating the reactor, and maintaining the temperature of the ore adjacent the upper portion of said bed sufficiently high to prevent condensation of iron chloride in said upper portion.

16. A continuous process of chlorinating an iron titanium ore containing at least about 20 percent titanium which comprises forming a pervious bed containing ore and carbon, passing chlorine through said bed at a temperature above about 700° C., and withdrawing vaporized chlorides from the surface of said bed, introducing further quantities of fresh ore and carbon upon said surface and maintaining the temperature of said surface above 300° C.

17. A continuous process of chlorinating a titanium bearing material containing at least about 20 percent of titanium which comprises forming a pervious bed containing said material, passing chlorine through the bed and maintaining the temperature above about 600° C., withdrawing vaporized chlorides from the bed, introducing a further quantity of fresh titanium bearing material and regulating the rate of introduction of said material to maintain a bed at least about 6 inches thick measured from the hottest portion of the bed to the top of the zone of chlorination.

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