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CHEMICAL PROCESS

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This invention relates to the treatment of titanium bearing materials. Titanium occurs widely in nature in the form of various titanium oxide bearing materials. Typical titanium ores are rutile, which usually contains in excess of about 90 percent of TiO_2, and ilmenite, which is an iron-titanium ore which contains in excess of about 10 percent by weight of titanium and 10 percent by weight of iron, both in the form of oxides, the titanium oxide usually being present as a mineral, $FeO.TiO_2$. In addition, there are other materials which contain in excess of about 10 percent by weight of titanium and 10 percent by weight of iron.

For many purposes, it is desired to subject to treatment materials which contain a maximum amount of titanium dioxide. Thus, in chlorination processes for the production of titanium tetrachloride, it is desirable to use rutile since the chlorination of other ores inevitably results in the chlorination of undue amounts of iron and possibly other components of the ore. This results in consumption of an undesirable amount of chlorine.

In many cases, it has been found desirable to beneficiate the ore prior to chlorination or other treatment. Thus, low grade ilmenite ore, such as occurs in large volume in Canada, has been subjected to a preliminary reduction with carbon (such as coal, coke, wood, carbon monoxide, etc.) in order to reduce a substantial portion of the iron to metallic state and to form a titanium-rich slag which is separated from the molten iron. This slag is a well-known material, frequently known as "QIT Slag" or "Sorel Slag." Other slags of similar composition may be obtained by heating ilmenite ore with carbon and wood chips, also to effect a partial reduction of the iron to metallic state and separation of a resulting slag from the molten metal. Other typical slags of this character are disclosed in U. S. Patent No. 2,476,453.

The total titanium content (TiO_2, TiO, and Ti_2O_3) of such slags, expressed as TiO_2, usually ranges from about 50 to 80 percent by weight of the slag, while the total iron, expressed as FeO, usually is 1 to 20 percent by weight. About 10 to 80 percent of the titanium is in trivalent and/or divalent state. The slags usually also contain substantial concentrations, ranging from 1 to 20 percent, of calcium, magnesium, and like alkaline earth metals as oxides which may be present as such or in combination with other materials such as silica.

Since the components other than the titanium oxide in such slags are chloridizable upon chlorination of the slag and therefore consume chlorine, further benefication of the slag is desirable to minimize the amount of chlorine used per pound of titanium tetrachloride produced.

According to the present invention, it has been found that such slags and like materials which contain divalent and/or trivalent titanium in addition to tetravalent titanium may be effectively beneficiated by oxidizing the slag to convert the lower valent titanium oxide compounds to tetravalent state, and holding the oxidized slag at an elevated temperature above 1000° C., and preferably above about 1350° C. up to just below the temperature at which the mixture becomes molten, until titanium dioxide crystals, usually rutile, are formed and grow. The slag should be held at this temperature long enough to grow rutile or like titanium dioxide crystals to appreciable size. After substantial growth of such crystals has taken place, the product is cooled and the rutile or like titanium dioxide is separated from one or more of the other components of the treated product.

The temperature at which the titanium dioxide crystals are grown normally ranges from about 1300 to 1600° C., but, in any event, should be low enough so that not more than a portion of the entire slag is molten. The oxidized slag is held in this temperature range for an appreciable period of time, usually in excess of 12 hours and frequently in excess of 48 hours, until appreciable growth of TiO_2 crystals has taken place. Other things being equal, the larger the crystal the easier the subsequent separation. Preferably, a majority of the rutile crystals produced should have a crystal size in excess of about 300 mesh (U. S. Standard screen size).

After the oxidized titanium slag has been thus treated, it is allowed to cool and separation of rutile from other component or components is conducted by various methods. In accordance with one method, the slag may be crushed to a suitable particle size, for example, minus 100 mesh or even as small as minus 300 mesh. Thereafter, the slag may be treated by electromagnetic separation methods to remove magnetic components, such as iron-containing substances, and/or may be treated by electrostatic methods to separate the siliceous components from the titanium dioxide (rutile) component. Thus, the pulverulent material may be passed over a magnet, and magnetic materials, such as iron oxide, separated from the titanium. Also, the product, when subjected to a high voltage electrostatic field, can be separated into two fractions according to known technique.

As an alternate or in conjunction with the electrostatic and/or electromagnetic processes, it is also possible to effect separation of the siliceous components, as well as the alkaline earth metal components, by a gravity separation. The alkaline earth metal component is found to be in the form of alkaline earth metal compounds (silicate or other form) which have a density substantially less than that of the rutile component. Therefore, when the slag, after grinding, is dispersed in an organic liquid having a density between that of the rutile and that of the siliceous alkaline earth metal compound, the siliceous material floats off and a titanium concentrate collects at the bottom of the liquid. Typical liquids of the type contemplated are methylene iodide and bromoform. Carbon tetrachloride is another liquid of this character which may be used either alone or in conjunction with methylene iodide or bromoform. Other liquids having a density in the range of about 3 to 3.3 are useful for this purpose.

The slags which are used in the process disclosed herein may be subjected to the treatment herein contemplated immediately after formation of the slag and removal of the iron therefrom. Thus, the molten slags which are tapped from the iron may be subjected to treatment as herein contemplated before they are allowed to cool below 1000° C. In such case, the slag is oxidized while in the molten or at least sintered state, and is held in insulated ladles in the molten or sintered state for the time required to cause crystal growth.

The oxidation of the slag is conducted by any convenient method which will convert the di- and trivalent titanium components predominantly or substantially wholly to tetravalent state. This may be accomplished by passing air through the slag while it is in either molten state or at a temperature above 1300° C. The oxidation may also be conducted by adding oxidizing agents, such as barium

peroxide, sodium peroxide, V_2O_5, or like inorganic peroxides, to molten slag prior to allowing the slag to cool to a temperature at which crystallization takes place. Slag which has been previously allowed to cool may be oxidized simply by subjecting it to an oxidizing roast in air or oxygen at any convenient temperature at which the oxidation can take place, usually above 500° C.

The following example is illustrative:

Example I

A quantity of "Sorel Slag," produced by smelting ilmenite ore in the presence of carbon and under reducing conditions to produce the slag and molten metallic iron, was heated at a temperature of 1410 to 1550° C. for 102 hours. Fifteen percent of the titanium in this slag was in a valent state below the tetravalent state. During the heating, air was allowed to pass through the slag so that the heating was conducted under essentially oxidizing conditions, and the titanium components were largely oxidized to tetravalent state before expiration of 5 to 10 hours of heating. Thereafter, the mixture was allowed to cool slowly at a relatively uniform rate over a period of 24 hours. The resulting product was crushed and screened to collect a fraction having a particle size of minus 150 and plus 200 mesh. This product contained well-formed, red-brown crystals, and white, transparent, and glassy particles.

A quantity of this material was dispersed in di-iodomethane, 10 cc. of di-iodomethane being used for 5.6 grams of the treated slag. A portion of the product floated on the surface of the di-iodomethane and was separated. The remainder sank to the bottom and was recovered by removal of the di-iodomethane. The portion which settled to the bottom was then passed through an electromagnetic separator and approximately 75 percent of the product was found to be nonmagnetic. The nonmagnetic fraction contained 83 percent by weight of TiO_2 and only about ½ percent by weight of CaO. This is about one-half of the original CaO concentration of the ore.

The above example is illustrative of the manner in which the process may be performed using slag which has been previously allowed to cool to room temperature. In this test, the temperature of the slag itself remained at about 1400° C. and thus was in a sintered rather than molten condition. If desired, the material may be melted prior to such treatment. In such a case, the temperature of the slag is raised higher, for example, 1600° C. or above, until the product becomes molten. Thereafter, it is allowed to cool until crystals begin to form and thereafter is held at the crystallizing temperature (about 1400 to 1600° C.) until an appreciable growth of the titanium dioxide crystals has taken place.

As explained above, the molten slag, immediately after formation and removal from molten iron, may be treated as herein contemplated.

The following examples are illustrative:

Example II

One hundred parts by weight of the slag described in Example I is heated to 1600° C. and air or pure oxygen bubbled through the melt until the titanium components are oxidized largely to tetravalent state. The mixture is cooled to the point where solid begins to form and held at a temperature above 1400° C. for 2 days. Thereafter, the product is cooled and the components are separated as in Example I.

Example III

The process of Example II is performed using the molten slag produced substantially according to the process described in U. S. Patent No. 2,476,453.

In the practice of the above examples, inorganic peroxides, such as barium peroxide or sodium peroxide, may be used in lieu of or in conjunction with oxygen to achieve the desired oxidation.

Although the present invention has been described with reference to the specific details of certain embodiments, 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.

What is claimed:

1. A method of beneficiating a titanium bearing slag which contains titanium in a tetravalent state, titanium in a valent state below the tetravalent state and iron and alkaline earth metal oxide impurities which comprises oxidizing the slag to effect substantially complete conversion of the titanium to tetravalent state, holding the oxidized slag at a temperature at which titanium dioxide rutile crystals are formed for a time to permit growth of such crystals thus separating rutile from said impurities, allowing the slag containing the titanium dioxide rutile crystals to cool thereby producing a mixture of said crystals and impurities, and subsequently separating impurity from such crystals.

2. A method of beneficiating a titanium bearing slag which contains as impurities an alkaline earth metal compound and iron and in which the titanium is present in a tetravalent state and in a valent state below the tetravalent state which comprises oxidizing the slag to effect substantially complete conversion of the titanium to tetravalent state, holding the oxidized slag at a temperature at which titanium dioxide rutile crystals are formed for a time to permit substantial growth of such crystals thus separating rutile from said impurities, allowing the slag containing the grown titanium dioxide rutile crystals to cool, and separating grown crystals from the resulting product.

3. A method of beneficiating a titanium bearing slag which contains titanium in a tetravalent state, titanium in a state below the tetravalent state and as impurities iron and alkaline earth metal oxide which comprises oxidizing the slag to effect substantially complete conversion of the titanium to tetravalent state, holding the oxidized slag at a temperature above 1400° C. at which titanium dioxide rutile crystals are formed for a time to permit growth of such crystals thus separating rutile from said impurities, allowing the slag containing the resulting titanium dioxide rutile crystals to cool and thereby producing a mixture of titanium dioxide rutile and impurities, and separating rutile from said impurities.

4. A method of beneficiating a titanium bearing slag which contains iron and alkaline earth metal oxide impurities, titanium in a tetravalent state, and titanium in a valent state below the tetravalent state, which comprises oxidizing the slag to substantially completely convert the lower valent titanium to tetravalent state, holding the oxidized slag at a temperature in the range of 1200 to 1600° C. at which titanium dioxide rutile crystals are formed for a time to permit growth of such crystals thus separating rutile from said impurities, allowing the slag containing the titanium dioxide rutile crystals to cool, and separating rutile from the resulting product.

5. A method of beneficiating a titanium bearing slag produced by melting ilmenite under reducing conditions and removing iron therefrom, which slag contains titanium in a tetravalent state as well as titanium in a valent state below the tetravalent state and as impurities iron and alkaline earth metal oxide which comprises oxidizing the slag to effect substantially complete conversion of the titanium to tetravalent state, holding the oxidized slag at a temperature at which titanium dioxide rutile crystals are formed for a time to permit substantial growth of such crystals thus separating rutile from said impurities, allowing the slag containing the grown titanium dioxide rutile crystals to cool, and separating rutile from the resulting product.

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