

REMOVAL OF RADIONUCLIDES FROM TITANIUM BEARING ORES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention provides an improved method for purifying titanium bearing materials which contain numerous impurities. More specifically, it relates to a process for removing radionuclide components from titanium bearing ores and other materials.

5 2. Description of the Prior Art

The purified titanium bearing materials produced by the method of this invention can be used to make titanium tetrachloride, which is widely used as a starting material for producing titanium dioxide pigments, metallic titanium, and organo titanium compounds. Currently, approximately 75 percent of the titanium minerals produced in the world are
10 utilized by the pigments industry in titanium dioxide form. In general, titanium tetrachloride is produced by a fluidization chlorinating process which comprises reacting a beneficiated titanium bearing material with chlorine gas at from about 800°C to about 1200°C in a chlorinator in which the material is maintained in a fluidized state. In the chlorination process, beneficiated ore is used which generally contains from about 55 to about 96 percent
15 titanium dioxide. The type material beneficiated, the nature of the impurities in the raw material, and the beneficiation process employed, will all influence the final concentration of the titanium dioxide in the beneficiated ore that is used in the chlorination process.

Known beneficiation processes have been developed, and are generally effective, to remove conventional metallic impurities such as iron from titanium bearing ores.

20 Beneficiation processes are not known, however, that are capable of satisfactorily and economically purifying titanium dioxide ores which contain radionuclide impurities such as

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thorium and uranium. These impurities cannot be readily removed by conventional chemical or mechanical means, and present a substantial health risk and risk to the environment.

Being able to remove radionuclide impurities efficiently would be highly desirable because known sources of titanium bearing ores not containing such impurities are increasingly becoming scarce and expensive. Conversely, there exist large bodies of rich, inexpensive ilmenite and carbonated anatase ores which contain such impurities.

Many processes are known for beneficiating titaniferous ores, and specifically ilmenite. Examples of such processes are disclosed in Von Bichowsky U.S. Patent No. 1,902,203, Dawson, et al., U.S. Patent No. 2,127,247, Pike U.S. Patent No. 2,903,341, and Aramendia, et al., U.S. Patent No. 3,457,037. The processes disclosed in these patents include the steps of reduction and leaching. Depending upon the amount of reduction, the iron compounds originally contained in the ilmenite, i.e., ferric and ferrous oxide, are reduced in various amounts to ferric and ferrous oxide and metallic iron. During the subsequent leaching step, the iron values are solubilized in varying amounts, leaving a residue which is rich in titanium dioxide.

The bulk of titanium ores today are beneficiated by the hydrochloric acid leaching process before undergoing chlorination. Because iron is the most prevalent and substantial impurity in nearly every titanium bearing ore mined today, the principal objective of the hydrochloric acid leaching process is to remove iron impurities from the ore. The hydrochloric acid leaching process for ilmenite ore involves four major steps as follows:

- (1) Pre-leaching treatment of ilmenite ore. Generally, this involves a reductive roasting of the ore at a temperature of from about 700°C to about 1200°C. The reductant used can be solid (such as coal, coke), or liquid (such as fuel oil) or gaseous (such as hydrogen, carbon monoxide), or a mixture of such reductants.

The degree of reduction can be partial -- just to reduce most of the ferric iron in the ore to the ferrous state. It can also be substantially complete -- to reduce most of the iron value all the way down to metallic iron.

In some processes, a pre-oxidation roasting to convert most of the iron value to the ferrous state is employed prior to the reductive roasting step.

(2) Hydrochloric Acid Leaching. Pre-treated ore such as ilmenite is mixed with a suitable amount (generally from about 15 percent to about 30 percent in excess of the stoichiometric requirement) of hydrochloric acid in a vessel where the reaction to dissolve the iron value and other impurities takes place with added heat and a suitable form of stirring or agitation of the contents.

A common concentration of the acid used is from about 18 percent to about 20 percent HCl, which is the usual concentration of the acid regenerated from the mother liquor. Other concentrations may be used, although they may not be economical. Leaching temperature may range from about 100°C to about 150°C, for a leaching period of from about six to about fourteen hours.

Leaching may be accomplished in one or more stages, batch or continuous, and at atmospheric pressure or greater, e.g., up to 50 PSIG. The total amount of hydrochloric acid used in all stages generally is from about 2 to about 3.8 parts per weight thereof per one part by weight of the ilmenite ore. When the desired degree of leaching is achieved, the mother liquor is separated by conventional means from the solid residue. The former is transferred to the acid regeneration system for the regeneration of HCl, while the latter is washed with water to practically free it from the mother liquor prior to calcination.

(3) Calcination of Leached Ilmenite. The wet solid residue after washing is calcined under a temperature of from about 700° to about 1200°C. The product,

beneficiated ilmenite or synthetic rutile, usually contains from about 90 percent to about 95 percent titanium dioxide depending on the composition of the original ilmenite used.

(4) Regeneration of Hydrochloric Acid. The mother liquor, containing mainly water, iron chlorides and some free HCl, is "spray roasted" in the presence of air whereby the iron chlorides are converted into HCl and to iron oxide. The regenerated HCl is absorbed in water to form about 18-20% HCl and recycled back into the leaching step. The iron oxide is a by-product.

Other processes are known as alternatives or improvements of the foregoing process for the removal of iron and other metallic values from titanium bearing ores.

U.S. Patent No. 4,176,159 discloses a process for the removal of impurities from rutile, ilmenite, and leucoxene ores. The process requires high temperature calcining, cooling, reducing, cooling, magnetic separation, mineral acid leaching, neutralizing, and washing.

U.S. Patent No. 4,562,048 discloses the beneficiation of titaniferous ores by leaching with a mineral acid. The temperature used is 120°-150°C, and the pressure used is 10-45 pounds per square inch gauge ("PSIG"). An essential aspect is the venting of water vapor generated during the leaching process. Prior to leaching, the ore is reduced at about 600°-1100°C.

U.S. Patent No. 4,321,236 discloses a process for beneficiating titaniferous ore. The process requires pre-heating the titaniferous ore and a mineral acid prior to the leaching operation. The temperature is maintained at 110°-150°C, and the pressure is maintained at 20-50 PSIG. For ores containing iron in the ferric state, reductive roasting at about 800°-1100° is suggested prior to leaching.

U.S. Patent No. 4,019,898 discloses the addition of a small amount of sulfuric acid to the leach liquor used to beneficiate ilmenite ore. The temperature used is 100°-150°C, and the pressure used is up to 50 PSIG. For ores containing iron in the ferric state, the ore is reduced prior to leaching at a temperature of about 700°-1200°C.

5 U.S. Patent No. 3,060,002 discloses acid leaching of ilmenite and Sorel slag at temperature of 150°-250°C. Prior to leaching, the ore preferably is roasted oxidatively at about 500°-1,000°C.

U.S. Patent No. 4,038,363 discloses upgrading of titanium values in a slag such as Sorel slag by roasting with an alkali salt, leaching with sulfuric acid in two stages, and
10 calcining.

Japanese Patent No. 48,102,712 discloses dephosphorization of titanium concentrates using caustic alkali after prior removal of iron.

Japanese Patent No. 87-33058/47 discloses production of rutile type titanium dioxide solids by heat treating hydrated titanium oxide and alkali metal hydroxide and maturing in
15 hydrochloric acid aqueous solution.

These prior art processes do not have as an objective the removal of radionuclide impurities such as thorium and uranium, and do not teach the removal of radionuclides. These known methods have, in fact, proven ineffective to substantially reduce radionuclide concentrations in titanium bearing ores having significant concentrations of radionuclides.
20 Since radioactivity must be minimized in order to reduce health effects from the use of a titanium bearing material with radionuclide impurities, standard corporate guidelines on radioactivity require synthetic rutile to contain no more than 100 ppm thorium and uranium. This is typically accomplished by mixing a beneficiated ore that is high in thorium and uranium with another ore that is low in thorium and uranium. Several recently issued patents

have also been directed toward improving radionuclide removal efficiencies in titanium bearing ore beneficiation processes.

U.S. Patent No. 5,181,956 discloses a process for removing radionuclides from titanium bearing ore which comprises reductive roasting followed by a leaching step, which
5 employs a mineral acid having a concentration of about 3-30% by weight at a temperature of about 160°-300°C, until the desired amount of impurities are solubilized and a leachate is formed, and then removing the leachate from the product of the contacting step. The process disclosed by U.S. Patent No. 5,181,956, has the obvious disadvantage of taking place after a reductive roast and under severe conditions that can quickly destroy or
10 degenerate process equipment.

U.S. Patent Nos. 5,011,666 and 5,085,837 disclose a process for removing radionuclides from titanium bearing ore consisting essentially of subjecting the ore to two or more leaching treatments, said leaching treatments alternating between use of an aqueous solution of a mineral acid and an aqueous solution of an alkaline metal compound selected
15 from the group consisting essentially of alkaline metal carbonates, hydroxides or mixtures thereof. The processes disclosed by U.S. Patent Nos. 5,011,666 and 5,085,837, do not adequately solve the problem of radionuclide removal because they require too many steps, and much investment in and reconfiguration of process equipment.

It has been found that if an ore is reduced at high temperatures to convert iron oxides
20 to metallic iron, and then the iron is removed from the pores in the ore particles by a nonaggressive reaction such as aeration in a 0.3 molar solution of ammonium chloride at ambient temperature to rust the iron, thorium is not removed from the surface of the ore. The thorium or other radionuclide ends up in the beneficiated ore. Based on these results it would appear that a more aggressive reaction would be needed to effectively remove the

radionuclide impurities. Indeed, U.S. Patent No. 5,181,596 discloses just such a method, by disclosing a process of a reductive roast followed by an acid leaching process at an elevated temperature between 160°C and 300°C to effectively remove the radionuclide impurities and to produce a sufficiently pure beneficiated ore.

SUMMARY OF THE INVENTION

It has been unexpectedly found, however, that the efficiency of radionuclide removal in a titanium bearing material beneficiation process can be substantially improved by subjecting the titanium bearing material to a preliminary leaching step, prior to reductive roasting, under mild conditions in a mineral acid bath, separating the mineral acid from the ore, and thereafter processing the ore according to any beneficiation process known to reduce the impurities remaining in the titanium bearing material. According to this invention, there is provided a process for purifying titanium ore and removing radionuclide impurities therefrom, comprising, prior to reductive roasting, leaching the ore advantageously at atmospheric pressure and at a temperature range from about 100°C to about 110°C, preferably at about 105°C in a mineral acid bath, of optimally 18 percent hydrochloric acid by weight, thereby solubilizing the radionuclide values in the ore; separating the mineral acid solution and solubilized radionuclide impurities from the ore; and further processing the ore according to beneficiation processes known to remove remaining impurities such as iron.

In accordance with this invention, it has been found that the aforementioned radionuclide impurities can be readily reduced to an acceptable level, especially when producing titanium dioxide by the chloride process. It also has been found that (1) relative to commercially available acids, dilute acids often can be used for the ore preleaching step which are less expensive and produce less amounts of waste streams than strong acids; and (2) mineral acid used in the ore preleaching step can be beneficially reused as the acid in a

subsequent acid leaching step if called for by the beneficiating process employed, which reduces the problem of disposing or regenerating such acids. Finally, the process of this invention is highly useful and desirable because it will make practical the utilization of low-grade, inexpensive and more abundant titanium dioxide ore which contains radionuclide impurities. The process is also simple and requires few steps.

DESCRIPTION OF THE DRAWING

Fig. 1 depicts a treatment process employing the subject invention in a typical titaniferous beneficiation process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of this invention can be practiced on any titanium bearing material in any form, including anatase, ilmenite and rutile. Preferred materials are titaniferous, such as ilmenite, titaniferous hematite, and titaniferous magnetite. Especially preferred is ilmenite. Because radionuclide impurities are most commonly associated with titaniferous ores such as ilmenite, leucoxene, rutile, perovskite, and sphene, the process can advantageously be applied to reduce radionuclide levels in these ores. As used herein, the term "ore" includes raw ore and beneficiates and derivatives thereof such as slag, blowover fines from titanium dioxide chlorinators, or other process streams from a titanium dioxide manufacturing process. The terms titanium dioxide ore, titanium bearing ore, and titanium bearing material, are all used interchangeably.

An ore from western Australia known commercially as TiWest ore is a typical titanium bearing ore that can be processed beneficially according to this invention. Such ore has the disadvantage of having a high concentration of thorium -- ranging from about 120 to about 170 ppm by weight. Thorium distributes itself between the synthetic rutile and iron

oxide products from the synthetic rutile process. Such ore normally contains less than about 10 ppm uranium.

Though the process of this invention is generally effective to remove radionuclides from all sizes of ore, the present invention is particularly effective for processing ores having
5 a particle size of from about 200 to about 20 mesh.

The impurities which can be removed in accordance with the process of this invention include but are not limited to radionuclides such as thorium and uranium. The process of this invention can be employed singularly to remove only the radionuclide impurities from the base material, or can be performed in conjunction with known beneficiation processes to
10 remove other impurities, such as, for example, iron, phosphorus, aluminum, manganese, calcium, barium, strontium, chromium, vanadium, yttrium, and lanthanide elements such as lanthanum, cerium, and neodymium. Examples of beneficiation processes to remove these elements are identified in the background section of this specification.

The invention comprises leaching the titanium bearing material in a mineral acid leach
15 prior to reductive roasting. Preferably the acid leach is performed as the first step of a known beneficiation process. A comminuting, sizing, or grinding process may be employed before the acid leach, to obtain the most effectively sized and shaped ore particles. Fig. 1 shows the initial step to remove the radionuclide impurities from a titanium bearing ore stream 11 taking place in step 12 before any roasting or leaching of the material to remove
20 other impurities in the ore as in steps 15 and 17.

The inventive leaching step 12 takes place at a temperature and pressure, and for a time, which is sufficient to solubilize substantially the radionuclide impurities present. Ordinarily, the time required will be at least about 1 hour. Typical ranges of time are from about 1 hour to about 6 hours, preferably from about 3 hours to about 6 hours, and most

preferably about 5 hours to about 6 hours. The temperature will advantageously be from about 100° to less than about 160°C, preferably from about 100° to about 110°C, and most preferably at about 105°C, the boiling point of 18 percent hydrochloric acid at atmospheric pressure. Although treatments at temperatures greater than 160°C have also proven effective
5 to remove radionuclides, operation of process equipment at greater than 160°C leads to rapid equipment degeneration.

The preliminary leaching step 12 can be performed at about atmospheric pressure. Additional pressurization can be added, if desired. Preferably, the pressure range will be from about 1 to about 5 atmospheres absolute, and most preferably at atmospheric pressure.
10 The leaching can be performed in one or more digestions, based on the desired rate of removal of radionuclide impurities, and the desired end concentration of radionuclide impurities in the ore.

It has been found that the temperature and pressure of the process step 12 should preferably be maintained at about the boiling point of the leach liquor. It is believed that
15 boiling the leach ensures mixing of the ore and leach, and facilitates interaction and reaction between the acid and radionuclide components. Operation of the inventive leaching step at the mineral acid boiling point adds the further advantage that the temperature is insufficient to attack the titanium portion of the ore to any substantive extent. In this manner the ore is best preserved for more effective processing by, for example, a successive reductive roasting
20 and leaching process to remove remaining impurities as shown in Figure 1, steps 15 and 17. Operation of the inventive leaching step at the mineral acid boiling point also has the advantage that it does not induce the significantly harsh conditions that can deteriorate process equipment.

It has also been found that by separating the radionuclide components from the ore before further aggressive treatments such as reductive roasting, the radionuclides are more effectively and completely removed from the titanium bearing material. The leachate can be removed by any suitable means, including filtrating, decanting, centrifuging, or use of a hydroclone or classifier. Depending on the process employed, wash water or very dilute HCl solution can be used to wash the ore.

A substantial benefit can be realized from this invention by reusing the acid solution separated from the ore in the initial leaching step, as illustrated by Stream 14 in Figure 1. Because very little of the ore other than the radionuclide content is attacked at the moderate temperature and pressure employed in the initial leaching step the acid removed from the initial leach should be nearly the same concentration as when it was originally introduced to the leaching step, without having gone through extensive regeneration treatment. This acid solution may, therefore, be introduced into a subsequent leaching step without any processing. Fig. 1 references a typical use of such acid, being used in a titaniferous ore beneficiation process employing a reductive roasting step before the subsequent leach.

Hydrochloric acid is the most especially preferred acid employed in the preliminary leaching step of this invention. Other acids such as sulfuric acid, nitric acid, and hydrofluoric acid, while they will solubilize the radionuclide values, are generally undesirable because they attack TiO_2 values.

Advantageously the acid concentration used in the preliminary leaching step is about 8 percent or greater by weight, based on the total weight of the solution. More advantageously, the acid will be present in an amount of from about 10 percent to about 30 percent by weight, based on the total weight of the solution. Because a preferred embodiment of the invention involves using regenerated HCl, preferably, the concentration

of the acid will be from about 15 percent to about 20 percent based on the total weight of the solution, which is the typical concentration of HCl in regenerated solution. An 18 percent concentration of hydrochloric acid is most preferred. The product obtained by use of this process contains significantly reduced radionuclide concentrations. Depending on the ore involved, the concentration HCl employed and the reaction conditions, the process removes greater than about 50 percent of the radionuclides present, preferably above about 75 percent, thereby reducing the radionuclide concentrations to generally below 50 ppm. Ore treated by the process of this invention can thereby be used, without undesirable health or environmental effects, in any process in which a beneficiated titanium bearing ore can be used.

Without wishing to be bound to any particular theory, it is believed that the process of this invention derives its utility from the molecular structure of the titanium bearing ore. A scanning electron microscope, using energy dispersive spectroscopy, has shown spots on the surface of untreated ore particles that contain high concentrations of thorium, uranium, and rare earths. This evidence indicates that the radionuclides are heterogeneously distributed on the ore surface and not homogeneously distributed throughout ore particles. This is in contrast to iron values which are known to be homogeneously distributed within the molecular lattice of titaniferous ores.

EXAMPLES

Example 1

Commercially available TiWest ilmenite ore concentrations are given before and after acid leaching at 105°C and atmospheric pressure using 18 percent HCl at 2.7 ml solution/g ore, employing two three hour digestions.

	<u>Impurity</u>	<u>Before</u>	<u>After</u>
	TiO ₂ %	64	68
	Fe ₂ O ₃ %	31	28
	ThO ₂ , ppm	135	38
5	U ₃ O ₈ , ppm	10	<5
	(Th+U), ppm	127	33

Example 2

Commercially available TiWest ilmenite ore concentrations are given before and after acid leaching at 140°C using 18 percent HCl at 2.7 ml solution/g ore in atmospheric pressure, employing two three hour reductions.

	<u>Impurity</u>	<u>Before</u>	<u>After</u>
	TiO ₂ %	66	68.2
	Fe ₂ O ₃ %	31.3	26.9
	ThO ₂ , ppm	164	10
15	U ₃ O ₈ , ppm	<5	<5
	(Th+U), ppm	149	9

Example 3

Commercially available TiWest ilmenite ore concentrations are given before and after acid leaching at 160°C using 18 percent HCl at 2.7 ml solution/g ore, in atmospheric pressure, employing two three hour reductions.

	<u>Impurity</u>	<u>Before</u>	<u>After</u>
	TiO ₂ %	66	70.1
	Fe ₂ O ₃ %	31.3	22.9
	ThO ₂ , ppm	164	8
25	U ₃ O ₈ , ppm	<5	<5
	(Th+U), ppm	149	7

The foregoing is considered as illustrative only of the principles of the invention.

Further, since numerous applications of the invention, and modifications thereof will readily

occur to those skilled in the art, it is not desired to limit the invention to the exact operation shown and described, and accordingly all suitable modifications and equivalents may be resorted to, falling within the scope of the invention as claimed.

What is claimed is:

1. An improved process for beneficiating a titanium bearing material which comprises the steps of reductively roasting the titanium bearing material followed by leaching in a mineral acid leach, wherein the improvement comprises subjecting the titanium bearing material to a heat treatment in an aqueous solution of a mineral acid to remove
5 radionuclide impurities before reductive roasting.

2. A process as in claim 1, wherein the titanium bearing material is ilmenite, leucoxene, high grade titanium ore, titanium slag, or synthetic rutile.

3. A process as in claim 1, wherein the titanium bearing material is titaniferous.

4. A process as in claim 1, wherein the titanium bearing material has a particle size of about 200 US mesh or larger.

5. A process as in claim 4, wherein the titanium bearing material has a particle size of from about 200 to about 20 US mesh.

6. A process as in claim 1, wherein the treatment time is at least about 1 hour.

7. A process as in claim 6, wherein the treatment time is from about 3 to about 6 hours:

8. A process as in claim 1, wherein the mineral acid is hydrochloric acid.

9. A process as in claim 1, wherein the concentration of the mineral acid is from about 8 percent to about 30 percent by weight.

10. A process as in claim 9, wherein the concentration of the mineral acid is from about 15 percent to about 20 percent by weight.

11. A process as in claim 8, wherein the concentration of the hydrochloric acid is about 18 percent by weight.



12. A process as in claim 1, wherein the heat treatment is carried out at a pressure between about one atmosphere and about five atmosphere.

13. A process as in claim 12, wherein the heat treatment is carried out at about atmospheric pressure.

14. A process as in claim 1, wherein the heat treatment is carried out at from about 100°C to less than about 160°C.

15. A process as in claim 1, wherein the heat treatment is carried out at from about 100°C to about 110°C.

16. A process as in claim 1, wherein the heat treatment is carried out at about 105°C.

17. A process as in claim 1, wherein the concentration of radionuclides is reduced by about 50 percent or more prior to reductive roasting.

18. A process as in claim 1 wherein the titanium bearing ore is titaniferous, the mineral acid is separated from the titanium bearing material after the radionuclides impurity removal treatment, followed by reductive roasting of the titanium bearing material, and subsequent leach of the titanium bearing material using the mineral acid previously separated
5 from the titanium bearing material.

19. An improved process for beneficiating a titanium bearing material containing from about 120 to about 180 ppm combined thorium and uranium which comprises the steps of reductively roasting the titanium bearing material followed by leaching in a mineral acid leach, wherein the improvement comprises subjecting the titanium bearing material to a heat
5 treatment in an aqueous solution of a mineral acid to remove radionuclide impurities prior to reductive roasting.

