

PATENT SPECIFICATION

(11) 1262401

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DRAWINGS ATTACHED

- (21) Application No. 17691/70 (22) Filed 14 April 1970
 (31) Convention Application No. 866548 (32) Filed 15 Oct. 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 2 Feb. 1972
 (51) International Classification C 22 b 3/00 C 01 g 23/04//49/02
 (52) Index at acceptance

CIN 212 213 251 261 269 274 275 27Y 337 340 347 348
 34X 34Y 354 357 358 35Y 367 406 407 408
 415 41X 42Y 432 433 435 440 448 449 501 504
 508 510 515 516 52Y 540 541 553 555 560 561
 564 567 577 578 580 588 589 592 593 594 597
 609 60X 619 61Y 620 622 626 62Y 630 632 636
 63X 642 663 66X 674 675 679 684 685 729
 730 73Y

C1A N13A



(54) BENEFICATION OF ILMENITE

(71) We, BENILITE CORPORATION OF AMERICA, a corporation of Delaware, having a place of business at 233, Broadway, New York, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a beneficiation process for ilmenite and other titaniferous ores and slags in which iron and other acid soluble constituents are extracted from the ores by leaching with hydrochloric acid. Examples of titaniferous ores other than ilmenite are ilmenite-magnetite, ilmenite-hematite, titaniferous magnetite, and titaniferous hematite.

20 Beneficiated ilmenite is also known as synthetic rutile or upgraded ilmenite and has a high titanium dioxide content and a low iron content and is particularly suitable as a raw material for the manufacture of titanium tetrachloride for titanium dioxide pigments and other titanium compounds by the "Chlorination" (or "Chloride") process. Natural rutile is in increasing demand and due to the limited world production and increasing costs, beneficiated ilmenite is therefore becoming of increasing importance as a substitute since there are large deposits of ilmenite all over the world and the titanium dioxide content can be enriched to the required value. Beneficiated ilmenite is also more versatile and has superior characteristics, particularly porosity thus increasing the reaction contact surface which is advantageous in the Chlorination process.

40 Commercial quantities of beneficiated ilmenite have been produced by processes in which the ore is leached with 31.5% by

weight (20°Be) hydrochloric acid. These processes have been found to be uneconomical and impracticable due to the high cost of production, particularly the heavy consumption of hydrochloric acid, and the waste disposal problems.

In a commercial process it is not practical to heat externally a large vessel or digester that is lined with acid-resistant bricks. In view of the corrosive nature of boiling hydrochloric acid, indirect heating of the digester in such a process is therefore possible only if very expensive materials such as tantalum or titanium are used to construct the digester. In practice the digester is usually constructed with less expensive materials such as acid-resistant bricks with a rubber lining and therefore indirect heating is not possible. As a result, heating in such processes using 31.5% by weight hydrochloric acid has normally been by injecting steam directly into the digester. The amount of steam which condenses is not controllable and therefore during the digestion the acid concentration varies with the result that the product is not uniform in quality.

It has therefore been necessary to find a better process by which the cost of beneficiation could be competitive with the price of natural rutile, and which would produce a product suitable for the manufacture of titanium compounds.

According to the present invention, in a process for the beneficiation of a titaniferous ore or slag which comprises leaching the ore or slag in a digester with hydrochloric acid leach liquor, the liquor is heated by feeding a vapour mixture, formed by distilling an azeotropic mixture of hydrochloric acid and water, into the digester, by which

means the hydrochloric acid content of the liquor is simultaneously replenished.

In carrying out the process according to the present invention, the ilmenite or other titaniferous ore, depending upon the ferric iron and ferrous iron content in the ore, may first be subjected to reduction using conventional reductive roasting processes, e.g. with coke at 815°C to 1,090°C in which most of the ferric iron is converted to ferrous iron. This roasting also breaks up the crystal lattice structure of the ore with the advantage that the iron in the ore is more readily accessible to the acid during the digestion process.

The ilmenite or other ore or slag, whether or not it has been prereduced, is charged into a digester vessel that is lined with suitable acid resisting material. An aqueous solution of hydrochloric acid is provided in the vessel and the azeotropic vapour mixture is fed into the liquor. Conveniently the digester rotates slowly during digestion.

The process is preferably carried out as a two stage countercurrent process with the ore being fed first to the first stage and then to the second stage and liquor being drawn from the second stage and fed to the first stage and then being passed through a recovery process to recover hydrochloric acid which may then be recycled to the second stage. Of course the process can also be carried out as a single stage process in which the liquor is taken off from the single stage, hydrochloric acid is recovered from it and recycled, as the leach liquor or to provide the vapour mixture. In a two stage process it is generally preferred that about half the leaching should be conducted in each stage, so that about half of the total acid requirement is supplied to the first stage while the other half is supplied to the second stage.

The constant boiling azeotropic mixture of hydrochloric acid varies according to the pressure. For example, at 760 millimeters mercury pressure the constant boiling acid contains 20.22% by weight hydrochloric acid and boils at 108.85°C; and at 1,000 millimeters mercury pressure, it contains 19.73% by weight hydrochloric acid and boils at 116.18°C; and at 1,200 millimeters mercury pressure, it contains 19.42% by weight hydrochloric acid and boils at 122.38°C. The azeotropic mixture cannot be concentrated by simple distillation. The result is that the vapour mixture being supplied to the liquor always contains about 20% by weight hydrochloric acid and naturally the liquor will tend to have the same concentration. During start up, when liquid hydrochloric acid is being supplied to the digester, it is therefore preferred to use a 20% by weight aqueous solution.

The azeotropic vapour mixture is conveniently generated simply by distillation of aqueous hydrochloric acid and the hydrochloric acid being distilled may conveniently

be derived from a recovery treatment on liquors produced by the process of the invention.

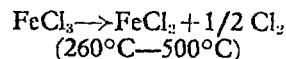
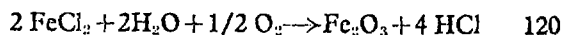
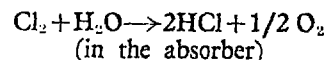
The total acid consumption, including hydrochloric acid condensed during digestion, for ilmenite of 55% to 60% by weight titanium dioxide content, is about 2.6 parts by weight of 20% by weight hydrochloric acid per 1 part of ilmenite. The actual consumption of acid for other types or qualities of ilmenite and other titaniferous ores would of course depend on the iron content and the acid soluble non-titanium values of the ore. However, in practice 15 to 20% by weight stoichiometric excess of acid should be provided for maximum extraction.

It is generally preferred that the leaching should proceed under a pressure of 20 to 50 p.s.i.g. and at an operating temperature in the range of 108 to 145°C. Under these operating conditions in a two stage countercurrent process each leaching stage would require about 5 hours, but the exact time cycle would depend on the type and properties of the raw material.

It is easily possible so to carry out the process of the invention that up to 94% by weight of the iron content in the original ilmenite or other ore or slag is dissolved in acid while the residue may contain up to 98% by weight of the titanium dioxide present in the original ore or slag.

The waste leach liquor obtained after the extraction process contains all the ferric chloride from the ore together with some free acid. Satisfactory recovery of the hydrochloric acid from this waste liquor makes an important contribution to the efficiency of the process according to the invention, since if the waste leach liquor was discarded it would not only create pollution problems but would make the process uneconomical. The recovery of the acid may be carried out by conventional processes such as the "Aman" process by Woodall-Duckham of England and the recovery plant by Dr. Otto and Company of Germany.

Basically the recovery processes generally involve hydrolysing metal chlorides at high temperatures by direct contact with combustion gases. The chemical reactions involved are:



The products of the reaction are therefore ferric oxide and aqueous hydrogen chloride which on distillation yields an azeotropic vapour mixture of about 20% by weight hydrochloric acid vapour.

The use of the azeotropic vapour mixture as the heating medium in the process of the invention has many advantages.

- 5 A particular advantage of using the azeotropic mixture of hydrochloric acid as the leach liquor is that the mixture has the maximum constant boiling point and thus the extraction process can operate at the highest temperature and lowest pressure. 20% by weight hydrochloric acid also provides the optimum rate of reaction, the reactivity being higher than more or less concentrated acids. Also at this concentration the loss of titanium dioxide in the waste leach liquor is minimised due to the fact that titanium dioxide dissolves more easily in weak acid solution at higher temperatures. The azeotropic mixture also has a very low partial pressure at boiling temperature which minimises the loss of acid due to vapourisation during digestion. Also it has the very important commercial advantages that it is the vapour mixture that is most easily obtained from the recovery process to which the liquors are subjected and recycling it reduces the consumption of acid. Also the process has the overall advantage that it avoids the disadvantages incurred previously by the use of steam heating.

- Equipment suitable for carrying out the cyclic process according to the invention for the beneficiation of ilmenite or other titaniferous ores is illustrated in the accompanying drawing. The leaching equipment illustrated is for a batch operation but continuously operating equipment can also be employed.

- In the drawing, 1 is a rotary spherical digester which is constructed of a mild steel body which is lined with rubber and covered with acid resistant bricks. It may, for example, have 16' O.D. in which event it will hold about 15 short tons ilmenite. 2 is a hydrochloric acid evaporator which is constructed of impervious graphite heating tubes for evaporating the acid with steam. 3 is a hydrochloric acid constant head tank which can be made of impervious graphite or 'Haveg' 41 (a reinforced phenol formaldehyde resin), which controls the acid level and separates the hydrochloric acid gas and liquid ('Haveg' is a Trade Mark). 20% by weight hydrochloric acid at about 91°C may be continuously fed into the evaporator to generate hydrochloric acid vapour which is used to heat up the digester. During digestion, pressure up to about 50 p.s.i.g. with corresponding temperature up to about 143°C. is maintained. After the digestion is complete the finished product is discharged from the man-hole into the pumping tank 4, in which it is mixed with water and pumped to a filter. The filtered product after washing free from hydrochloric acid is dried and may contain 90—95% by weight TiO_2 . The waste leach liquor mainly contains iron chlorides and a small amount of free hydrochloric acid and

is usually sent to a thickener, which is constructed of an acid proof material, to recover the fine slime of titanium dioxide. The clear waste leach solution is then pumped to the hydrochloric acid recovery unit for the regeneration and recovery of hydrochloric acid which can be reused for the digestion and/or for the vapourisation, thus completing the cycle of the process. The following is an example of the invention.

"Quilon" ilmenite (produced in India), having the following analysis by weight, was pre-reduced by heating with coke at about 900°C. for 40 minutes:

TiO_2	59.55%	80
Fe_2O_3	22.73%	
FeO	10.77%	
Al_2O_3	1.44%	
SiO_2	1.41%	
Others	balance	85

One part by weight of the pre-reduced ilmenite was leached in two stages with a total of 2.6 parts by weight (plus 15% excess) of pre-heated (100°C.) fresh HCl of 20% by weight strength, with 20% by weight vapour (108°C.) used for direct heating therein, each stage for 5 hours. After separation and drying, the beneficiated ilmenite had the following analysis by weight:

TiO_2	92.12%	95
Fe_2O_3	3.10%	
FeO	0.25%	

The beneficiated ilmenite to raw material weight ratio was 63.0:100. The amount of total iron extracted was 93.7% by weight and the amount of TiO_2 recovered 97.5% by weight.

WHAT WE CLAIM IS:—

1. A process for the beneficiation of a titaniferous ore or slag which comprises leaching the ore or slag in a digester with hydrochloric acid leach liquor, in which process the liquor is heated by feeding a vapour mixture, formed by distilling an azeotropic mixture of hydrochloric acid and water, into the digester, by which means the hydrochloric acid content of the liquor is simultaneously replenished.
2. A process according to claim 1 in which the titaniferous ore is ilmenite.
3. A process according to either preceding claim in which the leaching is conducted at a pressure of 20 to 50 p.s.i.g. and at a temperature of 108°C to 145°C.
4. A process according to claim 1 in which the hydrochloric acid in the liquor resulting from the leaching is recovered and is re-used in the process as hydrochloric acid leach liquor or is recycled to provide the vapour mixture.



The use of the azeotropic vapour mixture as the heating medium in the process of the invention has many advantages.

A particular advantage of using the azeotropic mixture of hydrochloric acid as the leach liquor is that the mixture has the maximum constant boiling point and thus the extraction process can operate at the highest temperature and lowest pressure. 20% by weight hydrochloric acid also provides the optimum rate of reaction, the reactivity being higher than more or less concentrated acids. Also at this concentration the loss of titanium dioxide in the waste leach liquor is minimised due to the fact that titanium dioxide dissolves more easily in weak acid solution at higher temperatures. The azeotropic mixture also has a very low partial pressure at boiling temperature which minimises the loss of acid due to vapourisation during digestion. Also it has the very important commercial advantages that it is the vapour mixture that is most easily obtained from the recovery process to which the liquors are subjected and recycling it reduces the consumption of acid. Also the process has the overall advantage that it avoids the disadvantages incurred previously by the use of steam heating.

Equipment suitable for carrying out the cyclic process according to the invention for the beneficiation of ilmenite or other titaniferous ores is illustrated in the accompanying drawing. The leaching equipment illustrated is for a batch operation but continuously operating equipment can also be employed.

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2. A process according to claim 1 in which the titaniferous ore is ilmenite.

3. A process according to either preceding claim in which the leaching is conducted at a pressure of 20 to 50 p.s.i.g. and at a temperature of 108°C to 145°C.

4. A process according to claim 1 in which the hydrochloric acid in the liquor resulting from the leaching is recovered and is re-used in the process as hydrochloric acid leach liquor or is recycled to provide the vapour mixture.



5. A process according to any preceding claim in which the leach liquor has a hydrochloric acid concentration of substantially 20% by weight.
- 5 6. A process according to any preceding claim in which the leaching is conducted in at least two countercurrent stages.
7. A process according to claim 1 substantially as hereinbefore described with reference to the accompanying drawing.
- 10 8. The product of a process according to any preceding claim.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.