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| (54) Title: PRODUCTION OF SYNTHETIC RUTILE (57) Abstract <p>The specification describes a process for producing synthetic rutile from a titaniferous ore or concentrate. The process involves three basic steps which are reduction, removal of iron by leaching or aeration and removal of other impurities by leaching in a solution of a strong mineral acid such as hydrochloric acid or sulphuric acid. The conditions of reduction are controlled to promote the formation of metallic iron, a major rutile phase and a minor impurity bearing phase. The minor impurity phase may be a metatitanate, an anosovite or a pseudobrookite. However, formation of a metatitanate is normally preferred. Suitable reductants include carbonaceous materials or hydrogen bearing gases such as natural gas or synthesis gas. The process is capable of removing more than 80 % of each of the contained iron magnesium and manganese remaining as oxides after reduction. Substantial proportions of contained aluminium can also be removed.</p> | | |

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- 1 -

PRODUCTION OF SYNTHETIC RUTILE

This invention relates to the treatment of titaniferous ores, for upgrading the titania content thereof.

In a particular embodiment the present invention provides a process for the removal of all or part of any iron, magnesium, manganese and aluminium from titanium bearing mineral ores or concentrates. In a general aspect the process of the invention comprises three basic steps, namely

- (i) a reduction step;
- (ii) a first stage leaching or aeration step, and;
- (iii) a second stage leaching step.

In step (i) the iron content of the titaniferous mineral is partially converted to metal by gaseous or carbothermic reduction.

In step (ii) the product of step (i) is subjected to an aqueous treatment, resulting either in the dissolution of the metallic iron content of the mineral or in the conversion of the metallic iron to a separable iron oxide product.

In step (iii) the titaniferous product of step (ii) is subjected to a leaching treatment, using one of a number of possible reagents, for at least partial removal of residual iron, magnesium, manganese and aluminium. The titaniferous product of leaching will then be of particularly high titania content and may be used in place of natural rutile or other high titania content materials.

Additional steps may be employed as will be described below.

In the prior art synthetic rutile has been formed from titaniferous minerals, e.g. ilmenite, via various techniques. According to the most commonly applied technique, as variously operated in Western Australia, the titaniferous mineral is reduced with coal or char in a rotary kiln, at

- 2 -

temperatures in excess of 1100°C. In this process the iron content of the mineral is substantially metallised. Sulphur additions are also made to convert manganese impurities to sulphides. Following reduction the metallised product is cooled, separated from associated char, and then subjected to aqueous aeration for removal of virtually all contained metallic iron as a separable fine iron oxide. The titaniferous product of separation is treated with 2 - 5% aqueous sulphuric acid for dissolution of manganese and some residual iron. There is no substantial removal of magnesium or aluminium from the product at any point in this process, and iron removal is only effected in the aeration step. After calcination the synthetic rutile contains approximately 92% TiO₂ and 1 - 2% iron as oxide.

The major use for synthetic rutile is as feedstock for the production of white titanium dioxide pigment via the chloride process. According to this process titania bearing minerals are charged with a carbon source to a fluidised bed chlorination reactor wherein gaseous titanium tetrachloride is formed. The titanium tetrachloride is subsequently condensed and purified and then is oxidised to titanium dioxide for use in pigments. The impurities iron, magnesium, manganese and aluminium in titaniferous feedstocks each have deleterious effects, either in chlorination, condensation or purification. Where a titaniferous mineral, such as ilmenite, has high levels of magnesium or aluminium it cannot be converted to a synthetic rutile by the Western Australian process which does not remove these impurities. Further, residual iron and manganese, as well as magnesium and aluminium, result in performance based penalties for synthetic rutile feedstocks to chlorination.

In other prior art inventions high degrees of removal of magnesium, manganese, iron and aluminium have been achieved. In one such process the ilmenite is first thermally reduced to substantially complete reduction of its ferric oxide content, normally in a rotary kiln. The cooled reduced

- 3 -

product is then leached under 35 psi pressure at 140 - 150° with excess 20% hydrochloric acid for removal of iron, magnesium, aluminium and manganese. The leach liquors are spray roasted for regeneration of hydrogen chloride, which is recirculated to the leaching step.

In other processes the ilmenite undergoes grain refinement by thermal oxidation followed by thermal reduction (either in a fluidised bed or a rotary kiln). The cooled, reduced product is then subjected to atmospheric leaching with excess 20% hydrochloric acid, for removal of the deleterious impurities. Acid regeneration is also performed by spray roasting in this process.

In yet another process ilmenite is thermally reduced (without metallisation) with carbon in a rotary kiln, followed by cooling in a nonoxidising atmosphere. The cooled, reduced product is leached under 20 - 30 psi gauge pressure at 130°C with 10 - 60% (typically 18 - 25%) sulphuric acid, in the presence of a seed material which assists hydrolysis of dissolved titania, and consequently assists leaching of impurities. Hydrochloric acid usage in place of sulphuric acid has also been claimed for this process.

The major disadvantage of all processes using hydrochloric acid leaching for the formation of synthetic rutile from iron bearing titaniferous minerals such as ilmenite is the need to operate acid regeneration from the chloride liquors formed in leaching. Such acid regeneration requires combustion of large quantities of fuel to provide the necessary heat. The cost of synthetic rutile production by these methods, which are applicable to more general titaniferous minerals due to the ability to remove impurities, is uncompetitive with the reduction/aeration process operated in Western Australia. The major reason for this cost disadvantage is the formation of large quantities of iron chlorides in the process of impurity removal, placing a consequent heavy load on the acid regeneration system.

SUBSTITUTE SHEET

- 4 -

The major disadvantage of processes using sulphuric acid for the formation of synthetic rutile from iron bearing titaniferous minerals such as ilmenite is the need to dispose of aqueous iron sulphates (and other sulphates) from the liquors formed in leaching, in the absence of a by-product use for such liquors. Neutralisation with lime, producing large quantities of red gypsum, which must be disposed of in managed land based repository, will normally be necessary.

In summary, existing processes for the formation of synthetic rutile products from titaniferous minerals such as ilmenite will either not be effective in the removal of deleterious impurities or will not be cost effective due to the need to regenerate large quantities of expensive reagents or to neutralise and dispose of large volumes of leachate liquors. It is the object of the present invention to overcome, or at least alleviate some of these difficulties.

Accordingly, the present invention provides a process for upgrading the titania content of a titaniferous ore or concentrate which process comprises the steps of:

- (i) reducing the titaniferous ore or concentrate under conditions which promote the formation of metallic iron, a major rutile phase and a minor impurity bearing phase;
- (ii) cooling the product of step (i) in an oxygen free environment;
- (iii) subjecting the cooled product of step (i) to a first stage leaching or aeration to convert metallised iron into a readily removable form;
- (iv) removing iron from the product of step (iii);
- (v) subjecting the product of step (iv) to a second stage leaching to convert other impurity elements to a readily removable form; and
- (vi) removing the other impurity elements from the product of step (v).

- 5 -

In the process the iron present in the titaniferous mineral may be partially reduced to metallic iron by coke, char or coal, gaseous fuels such as hydrogen, natural and petroleum gas or products thereof, or liquid fuels such as oil or products thereof. The temperature of reduction should be above 900°C in the case of solid carbonaceous reductants and above 600°C in the case of hydrogen bearing gaseous reductants. For each mineral the optimum temperature of reduction will depend on the level of impurities present and the reductant used. In general, conditions should be set such that the predominant titanium bearing phase in the mineral after reduction is rutile or reduced rutile, while magnesium, manganese and residual (non-metallised) iron are predominantly concentrated into a small amount of a separate phase. This separate phase may have either the anosovite/pseudobrookite " M_3O_5 " structure or an ilmenite-like " M_2O_3 " structure. The latter structure is advantageous in subsequent steps of the process.

Reduction may be carried out in any suitable device including fluidised beds and rotary kilns. The presently preferred apparatus is a rotary kiln charged with solid carbonaceous reductant such as coal, char or coke and operated with a maximum temperature in the range 950 - 1050°C. However, higher temperatures may be operated, especially for ilmenites having low levels of impurities. It is not anticipated that the process would be operated at temperatures in excess of 1200°C due to the unavoidable formation of large quantities of non rutile phases, particularly M_3O_5 , and a tendency for the mineral to sinter and accrete at higher temperatures. The formation of appreciable quantities of non-rutile phases may result in low selectivity of impurity removal in the final leaching step of the process due to the dissolution of solubilised titania. Formation of M_3O_5 in preference to M_2O_3 will result in a need to use more aggressive conditions (higher acid strength, temperature and time) in leaching, which may be difficult to apply in practice.

SUBSTITUTE SHEET

- 6 -

The degree of conversion of the titaniferous mineral iron content to metal is not a critical part of the process provided that the sought after phases are produced in reduction. The optimum degree of metallisation will be
5 determined primarily by economic considerations in most circumstances. In general, degrees of metallisation in the range 50 - 95%, depending on mineral composition, will be suitable. A suitable degree of metallisation can be achieved in residence times from 30 minutes to several hours at or
10 above 900°C for carbothermic reduction in a rotary kiln. Actual metallisation for a given reduction time and temperature will depend on the nature of the mineral and the nature of the reductant (e.g. on carbon reactivity).

After reduction and the attainment of the desired degree of
15 metallisation, the material being heated must be cooled almost to room temperature in an essentially oxygen free environment. Cooling may be conducted in a cooler which forms an integral part of the reduction unit or in a separate cooling unit in an atmosphere of inert gases or reduction
20 product gases.

Separations of carbonaceous material from minerals may then be performed by a suitable combination of magnetic and size separations, with the carbonaceous component recirculated, as appropriate.

25 Metal may be removed from the cooled mineral particles by any suitable means. Aqueous chemical methods are most suitable. Acid leaching using any commercially available acid is effective in removing iron but results in iron salts in solution. The resulting solution will normally require iron
30 precipitation by neutralisation, spray roasting to iron oxide for acid recovery, or some other means of further treatment to avoid the need for disposal of environmentally harmful wastes. The most advantageous method for iron metal removal is aqueous aeration, in which air is blown through an
35 agitated aqueous suspension of metallised mineral in the

- 7 -

presence of added reagents such as ammonium chloride. Iron metal is converted to iron oxides according to this method. This technique is well known in the prior art. By adjustment of conditions the nature of the iron oxide product of aeration can be altered and its formation as a separable, finely grained suspension can be ensured.

Following aeration, separation of the titaniferous product from the iron oxides can be effected by any suitable method of sizing separation, such as by passage through cyclone separators. The coarser titaniferous product may then be dewatered by any suitable technique or combination of techniques, e.g. thickening and filtration.

The dewatered titaniferous product of aqueous chemical treatment according to the described process contains virtually all of its original magnesium, manganese and aluminium, and may have substantial quantities of residual iron oxides which were previously not metallised or have adhered during an aeration step. It has been found that leaching with strong acid is effective in the removal of these impurities, provided that appropriate conditions have been used in reduction.

Acid leaching using strong mineral acids under agitated conditions may be applied to impurity removal. For example, both sulphuric and hydrochloric acids have been shown to be effective. Prior to leaching it may be advantageous to grind the titaniferous mineral to assist leaching kinetics, although this step is not essential to the process. Leaching with excess 18 - 20 wt% HCl has been found to be particularly advantageous, and is preferred although lower concentration of acid (e.g. down to 4 wt %) have also been found to be effective.

Acid leaching may be conducted in any suitable batch or continuous leach vessel. For example, heated, agitated vessels or fluidised bed vessels may be used. Typically the

SUBSTITUTE SHEET

- 8 -

leaching temperature will be 80 - 150°C, depending on the leachant. Leaching may be conducted wither at atmospheric or at elevated pressures, although a feature of the present invention is the ability to operate the leach step without
5 the need for pressure vessels. Leaching time may be from 15 minutes to 24 hours, depending on the phase assemblage present in the reduced mineral and the desired degree of impurity removal. Greater than 80% removal of each of iron, magnesium, manganese, partial removal of aluminium may be
10 easily achieved by the described process.

At the conclusion of leaching the leach liquor may be separated from the mineral by any suitable means including thickening, washing and filtration. The mineral product is then dried and calcined for removal of moisture and
15 chemically combined water.

Calcination at temperatures in the range 300 - 900°C has been found to be effective. The resulting synthetic rutile product will contain greater than 90% TiO_2 and up to 99% TiO_2 , depending on the level of impurities in the original
20 titaniferous mineral grains, and the presence of non titaniferous grains in the original mineral which are retained through the process.

Additional steps may be incorporated in the process, as desired. For example:

- 25 (1) The original titaniferous mineral may be agglomerated prior to reduction, with or without pregrinding, by any suitable technique. In this manner a size consist which most suits the process dynamics of subsequent steps, e.g. reduction, may
30 be obtained.
- (2) Additives, such as chlorides or oxides (e.g. MnO_2), may be mixed into the titaniferous mineral prior to reduction in order to redistribute the metallic

- 9 -

iron produced via segregation reactions, thereby influencing metallic iron removal, or to encourage the formation of an acid leachable minor impurity bearing phase.

- 5 (3) The titaniferous mineral, or admixture containing the titaniferous mineral may be oxidised at elevated temperatures, preferably in excess of 700°C, to provide a degree of preheat to the mineral prior to reduction, and to enhance the rate and extent of the reduction reaction.
- 10
- (4) Following reduction the cooled, partially metallised mineral may be subjected to magnetic or other separation procedure for removal of impurity grains which do not metallise. Grinding prior to such separation may be operated with the objective of liberation of impurity grains from titaniferous grains.
- 15
- (5) Mineral separations based on magnetic separation, gravity separation, flotation or any other separation technique may be performed either after removal of metallic iron from the reduced mineral or after final acid leaching and/or calcination. In this manner impurity grains e.g. chromite may be removed.
- 20
- 25 (6) The final titaniferous product may be agglomerated, with or without pregrinding, by any suitable technique, to product a size consist which is suitable to the market for synthetic rutile. After agglomeration the product may be fired at
- 30 temperatures sufficient to produce sintered bonds, thereby removing from dusting losses in subsequent applications. Firing in this manner may remove from the need for product calcination.

SUBSTITUTE SHEET

- 10 -

(7) Leaching may be conducted either batch-wise or continuously, or in multiple co-current or countercurrent (in relation to solids and liquid flows) stages.

5 Within the disclosed process there is great flexibility in relation to the degree of iron removal in the first and second stages of aqueous treatment, and therefore the acid recovery or neutralisation costs. For many titaniferous feeds higher degrees of metallisation in reduction will
10 correspond to greater difficulty of subsequent impurity removal in acid leaching due to the stabilisation of impurities in the less reactive anosovite phase. Consequently, an optimum balance between leach liquor treatment costs and difficulty of impurity removal may be
15 struck, depending on the economic environment.

Examples: The following examples describe a number of laboratory and pilot scale tests which serve to illustrate the techniques disclosed herein.

Example 1:

20 300 g of ilmenite in the size range 45 - 65µm having the composition given in Table 1 was mixed in equal weight proportions with Victorian brown coal char and placed in a 50mm I.D. lidded stainless steel pot. This pot was then situated in a 950°C muffle furnace for 3.5 hours, after which
25 time is was removed and allowed to cool.

The cooled mineral product was separated from associated char by magnetic separation, and then leached for removal of metallic iron with excess 5% sulphuric acid for 90 minutes.

30 In this step 89% of the iron content of the reduced mineral was removed into solution. The solids residue was filtered away from the liquor and then leached with refluxing 50 wt % sulphuric acid for 24 hours. The rate of removal of magnesium is indicated by Figure 1. After 24 hours of

- 11 -

leaching the leached solids contained 0.77% MgO, compared with an initial 2.25% (dry basis). However, approximately 15% of the titania was also taken into solution.

Example 2:

5 1 kg of agglomerated ilmenite ($-710 + 250 \mu\text{m}$) having the composition given in Table 1, was mixed in equal weight proportions with Victorian brown coal char ($-7 + 5\text{mm}$) and heated to 1000°C under 0.3m sec^{-1} nitrogen superficial velocity in a fluidised bed reactor. Upon reaching
10 temperature an 0.3 sec^{-1} superficial velocity flow of 50% hydrogen/50% carbon monoxide fluidising gas was commenced and maintained for a total of 4 hours. At the end of this time the bed was permitted to cool under nitrogen flow and the bed was separated magnetically and by sizing into char and
15 mineral. Chemical analysis indicated that the mineral was 95% metallised.

A 1g sample of reduced mineral was leached with 5 wt % sulphuric acid to the point of complete removal of metallic iron. The solids residue was then leached with excess
20 boiling 20 wt % HCl solution under reflux for 31 hours. The removal of various elements from the mineral is summarised in the following table:

| Element | Mg | Ti | Mn | Fe | Al |
|-----------|------|-----|------|------|------|
| % Removal | 96.1 | 9.0 | 99.6 | 97.9 | 80.3 |

25 Example 3:

A 2.6:1(wt basis) Victorian brown coal char ($-5\text{mm} + 0.5\text{mm}$)/agglomerated ilmenite (Table 1 : $-4\text{mm} + 250\mu\text{m}$) mixture was fed continuously at 18 kg/hr to an inclined 0.4m internal diameter, 5m long rotary kiln. The kiln was fired from the
30 discharge end with a gas burner, and combustibles in the above-bed gas space were combusted by injection of air at controlled rates via air lances at points along the kiln length. The kiln solids bed temperature profile increased uniformly from 200°C to 1000°C over the length of the kiln
35 from the charge point to the discharge. Total solids

- 12 -

residence time was estimated at 4 hours over this length. The kiln discharge was cooled to room temperature through a spiral cooler. A 300g sample of cooled kiln discharge was magnetically separated for char removal. A subsample of the magnetic product was analysed by X-ray diffraction, indicating major rutile and metallic iron phases, with minor quantities of the impurity bearing phases anosovite - pseudobrookite and ilmenite-like metatitanate occurring in roughly equal proportions. A further subsample was subjected to analysis for degree of metallisation by measurement of the magnetic attractive force on the sample in a saturating magnetic field against a known calibration. The indicated degree to which iron had been converted to metal was 78.3%.

A further 5g subsample of the magnetic product was subjected to 5 wt % sulphuric acid and 20% hydrochloric acid leaches as described in the previous example. After four hours of the final leach virtually all of the ilmenite-like metatitanate phase had been removed, while most of the anosovite/pseudobrookite phase remained. According to this example the formation of the ilmenite-like metatitanate residual phase is to be encouraged as it is more readily leached, with consequent removal of associated impurities.

Example 4:

Ilmenite of the composition provided in Table 2 and in the size range $-250\mu\text{m} + 100\mu\text{m}$ was treated through the rotary kiln of Example 3 in a similar manner to that specified above, with the exception that a flat temperature profile, at 950 $^{\circ}\text{C}$, was maintained over the final 2 metres of kiln length.

X-ray diffraction analysis confirmed that for this ilmenite at degrees of metallisation in excess of 90% the residual impurity bearing phase in the product reduced in this manner was predominantly metatitanate. It is apparent that at greater levels of impurities, as for the ilmenite of Table 1,

- 13 -

the anosovite-pseudobrookite phase is more favoured, requiring reduction at lower temperatures if the more readily leached metatitanate phase is desired.

Example 5:

- 5 Two 3 kg batches of -65 + 45 μ m ilmenite having the composition recorded in Table 3 were mixed with 1.5kg of -4 + 1.4mm Victorian brown coal char and placed in a muffle furnace for heating to a final steady state bed temperature of 1000 5°C.
- 10 The first batch was held above 900°C (metallisation initiation temperature) for 5 hours, while the second batch was held above 900°C for 3 hours. The batches were removed for cooling in air at the end of the heating period.

15 Magnetic separation was performed on the products of such reduction for removal of char, and the degree of metallisation of contained iron was recorded for the magnetic fraction as follows:

| | | % metallisation |
|----|---------|-----------------|
| | Batch 1 | 87 |
| 20 | Batch 2 | 47 |

25 The metallised minerals were subjected to iron metal removal by leaching with excess 5 wt % H₂SO₄ for 90 minutes at 80°C, before filtration, washing and drying to recover leached solids. X-ray diffraction analysis indicated the following phase distributions:

| | Batch 1 | Batch 2 |
|-------------------------------|---------|---------|
| Rutile | 44% | 32% |
| M ₃ O ₅ | 30% | 10% |
| M ₂ O ₃ | 12% | 43% |

- 30 The above materials were each subjected to leaching with refluxing excess 20 wt % hydrochloric acid for 6 hours. Extractions of residual impurities from the already

- 14 -

demetallised material were as follows:

| | | | |
|---|-----------|---------|---------|
| | % Removal | Batch 1 | Batch 2 |
| | Iron | 41.4 | 96.5 |
| | Manganese | 14.3 | 88.9 |
| 5 | Magnesium | 27.8 | 80.9 |
| | Aluminium | 17.1 | 18.0 |

Titanium extraction was negligible in each case.

X-ray diffraction analysis of the residues in each case indicated complete removal of the ilmenite, with slight removal of the M_3O_5 phase in the case of batch 2, but no M_3O_5 removal in the case of batch 1.

Samples of each of the demetallised materials were also subjected to leaching with excess refluxing 50% sulphuric acid for up to 24 hours. Extractions of residual impurities in the leaches after one hour were as follows:

| | | | |
|----|-----------|---------|---------|
| | % Removal | Batch 1 | Batch 2 |
| | Iron | 88.4 | 95.7 |
| | Manganese | 81.7 | 86.0 |
| | Magnesium | 75.5 | 85.7 |
| 20 | Aluminium | 26.1 | 24.9 |

Titanium extraction after one hour in the above cases was high (e.g. 20%) but hydrolysis of dissolved titania occurred over time in the leach to result in losses as low as 0.3%.

X-ray diffraction analysis of the residues in each case indicated virtually complete digestion of both M_2O_3 and M_3O_5 residual phases.

Example 6:

A 5 kg charge of ilmenite ($-65 + 35\mu\text{m}$) having the composition provided in Table 4 was fluidised with air at a superficial velocity of 30cm sec^{-1} (at temperature) in an external heated oxidising fluid bed roast conducted at 900°C for 30 minutes.

- 15 -

The temperature of the fluidised bed was then allowed to fall to 750°C and the bed was purged with nitrogen at 30cm sec⁻¹ fluidising velocity for 30 minutes. The fluidising gas was then replaced with hydrogen at a superficial velocity of 64cm sec⁻¹. Hydrogen reduction continued for 160 minutes, after which time the hydrogen was replaced with a purge of nitrogen and the bed was allowed to cool.

Analysis of the reduced ilmenite product indicated that 76% of its contained iron was metallised. This metallisation was removed by a 90 minute leach in 5 wt % H₂SO₄ at 80°C. The filtered and dried leach residue was then subjected to a further leach with excess 8.7 wt % hydrochloric acid/100 gram per litre ferrous chloride leachant, under reflux conditions. Extraction of residual impurities in the final leach were as follows:

| | % Removal |
|-----------|-----------|
| Iron | 98.7 |
| Manganese | 99.2 |
| Magnesium | 99.0 |
| Aluminium | 13.8 |

X-ray diffraction analysis of demetallised and residue samples indicated that the only residual impurity bearing phase in the demetallised sample was M₂O₃ and that this phase was entirely removed by the final leach.

Example 7:

Two kilograms of the ilmenite used in example 6 (see Table 4) was oxidised in a rotation pot inserted into a laboratory muffle furnace, at 1000°C in the presence of excess air. The oxidised ilmenite was allowed to cool, and then mixed 1:1 (weight basis) with Victorian brown coal char (-5 + 0.5mm). The mixture was then held for one hour in the absence of air in the rotating pot assembly with the furnace set at 950°C, and then allowed to cool.

- 16 -

Char was separated from the cooled mixture by magnetic separation and screening. The iron content of the separated reduced ilmenite was found to be 79.2% metallised.

Metallic iron was removed by a 90 minute leach in 5 wt %

- 5 H_2SO_4 at 80°C . The filtered and dried leach residue was then subjected to further leaches as follows:

Leach 1: Excess 18.5 wt % HCl for 6 hours at 104°C

Leach 2: Excess 20 wt % H_2SO_4 for 6 hours at 130°C under pressure.

- 10 Extraction of residual impurities from demetallised samples were as follows:

| | | % Removal | |
|----|-----------|----------------|----------------|
| | | <u>Leach 1</u> | <u>Leach 2</u> |
| | Iron | 77.5 | 88.1 |
| 15 | Manganese | 78.9 | 90.3 |
| | Magnesium | 81.2 | 91.7 |
| | Aluminium | 29.6 | 45.5 |

- 20 X-ray diffraction analysis of residue samples indicated that the M_2O_3 (predominant impurity bearing phase) was completely removed by both leaches while Leach 2, with sulphuric acid, also removed most of the M_3O_5 phase. Only approximately 4% of the contained titania was dissolved in each of the leaches.

- 17 -

Table 1: Composition of Ilmenite in Examples 1 - 3

| | | wt % |
|----|--------------------------------|------|
| | FeO | 9.68 |
| | Fe ₂ O ₃ | 25.3 |
| 5 | TiO ₂ | 53.4 |
| | Cr ₂ O ₃ | 0.62 |
| | SiO ₂ | 1.60 |
| | Al ₂ O ₃ | 1.94 |
| | CaO | 0.06 |
| 10 | MgO | 1.48 |
| | MnO | 1.23 |
| | V ₂ O ₅ | 0.25 |
| | ZrO ₂ | 0.17 |
| | P ₂ O ₅ | 0.46 |

15 Table 2: Composition of Ilmenite in Example 4

| | | wt % |
|----|--------------------------------|------|
| | FeO | 23.2 |
| | Fe ₂ O ₃ | 16.8 |
| | TiO ₂ | 53.8 |
| 20 | Cr ₂ O ₃ | 0.05 |
| | SiO ₂ | 0.68 |
| | Al ₂ O ₃ | 0.84 |
| | CaO | 0.26 |
| | MgO | 0.34 |
| 25 | MnO | 1.50 |
| | V ₂ O ₅ | 0.14 |
| | ZrO ₂ | 0.07 |
| | P ₂ O ₅ | 0.06 |

SUBSTITUTE SHEET

- 18 -

Table 3: Composition of Ilmenite in Example 5

| | | wt % |
|----|--------------------------------|------|
| | FeO | 10.5 |
| | Fe ₂ O ₃ | 23.6 |
| 5 | TiO ₂ | 51.4 |
| | Cr ₂ O ₃ | 1.01 |
| | SiO ₂ | 1.23 |
| | Al ₂ O ₃ | 1.22 |
| | CaO | 0.11 |
| 10 | MgO | 1.60 |
| | MnO | 1.19 |
| | V ₂ O ₅ | 0.25 |
| | ZrO ₂ | 0.73 |
| | P ₂ O ₅ | 1.55 |

15 Table 4: Composition of Ilmenite in Example 6

| | | wt % |
|----|--------------------------------|------|
| | FeO | 8.76 |
| | Fe ₂ O ₃ | 26.2 |
| | TiO ₂ | 57.3 |
| 20 | Cr ₂ O ₃ | 0.54 |
| | SiO ₂ | 1.16 |
| | Al ₂ O ₃ | 0.65 |
| | CaO | 0.05 |
| | MgO | 1.40 |
| 25 | MnO | 1.30 |
| | V ₂ O ₅ | 0.25 |
| | ZrO ₂ | 0.15 |
| | P ₂ O ₅ | 0.05 |
| | LOI | 0.71 |

SUBSTITUTE SHEET

- 19 -

CLAIMS

1 A process for upgrading the titania content of a titaniferous ore or concentrate which process comprises the steps of:-

- 5 (i) reducing the titaniferous ore or concentrate under conditions which promote the formation of metallic, iron, a major rutile phase and a minor impurity bearing phase;
- 10 (ii) cooling the product of step (i) in an oxygen free environment;
- (iii) subjecting the cooled product of step (i) to a first stage leaching or aeration to convert metallised iron into a readily removable form;
- 15 (iv) removing leached or aerated iron from the product of step (iii);
- (v) subjecting the product of step (iv) to further leaching processes to convert other
- 20 impurity elements to a readily removable form; and
- (vi) removing the other impurity elements from the product of step (v).

2. A process according to claim 1 wherein the minor impurity bearing phase is metatitanate (M_2O_3) or anosovite/pseudobrookite like phase (M_3O_5).

25

3. A process according to claim 1 or claim 2 wherein step (iii) comprises blowing air through an agitated aqueous suspension of the cooled product of step (i) in the presence

30 of an agent that promotes the formation of oxides of iron.

4. A process according to claim 1 or claim 2 wherein step (iii) comprises leaching the cooled product of step (i) in a solution of a strong mineral acid.

5. A process according to any one of the preceding

SUBSTITUTE SHEET

- 20 -

claims wherein step (v) comprises leaching the product of step (iv) in an agitated solution of a strong mineral acid.

6. A process according to claim 5 wherein the solution of strong mineral acid has an initial concentration in the range from 4 to 50 wt %.
7. A process according to claim 5 or claim 6 wherein the solution of strong mineral acid is maintained at a temperature in the range from 80 to 150°C.
8. A process according to claim 7 wherein the solution of strong mineral acid is refluxed.
9. A process according to any one of claims 4 to 8 wherein the strong mineral acid is hydrochloric acid or sulphuric acid.
10. A process according to any one of the preceding claims wherein step (i) comprises reducing the titaniferous ore or concentrate with a solid carbonaceous reductant at a temperature in the range from 900°C to 1200°C.
11. A process according to claim 10 wherein step (i) is performed at a temperature in the range from 900°C to 1050°C.
12. A process according to any one of claims 1 to 9 wherein step (i) comprises reducing the titaniferous ore or concentrate with a hydrogen bearing gaseous reductant at a temperature in the range from 600°C to 1200°C.
13. A process according to any one of the preceding claims wherein the process includes the preliminary step of oxidising the titaniferous ore or concentrate at a temperature in excess of 700°C.
14. A process according to claim 1 wherein the minor impurity bearing phase is anosovite or pseudobrookite and

SUBSTITUTE SHEET

- 21 -

step (v) comprising leaching the product of step (iv) in excess sulphuric acid whilst agitating the heated sulphuric acid for a period of from 15 minutes to 24 hours.

15. A process according to claim 14 wherein the acid
5 has an initial concentration of up to 50 wt %.

16. A process according to claim 1 wherein carbonaceous reductant is a sub-bituminous or lignitic coal or char derived therefrom.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 91/00069

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.⁵ C22B 34/12 // C22B 5/10, 5/12, 9/05, 3/06, 3/08, 3/10

II. FIELDS SEARCHED

Minimum Documentation Searched 7

| Classification System | Classification Symbols |
|--|---|
| IPC | C22B 5/10, 5/12, 3/00, 3/06, 3/08, 3/10, 34/12, 53/00 |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8 | |
| AU : IPC as above | |

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

| Category* | Citation of Document, with indication, where appropriate, of the relevant passages 12 | Relevant to Claim No 13 |
|-----------|---|-------------------------|
| X | Derwent Soviet Inventions Illustrated, Section I Chemical, Issued April 1966, General Inorganic, etc, p.4, SU 174363 (BORODAI, V.V. et al) February 1966 (00.02.66) | (1,4-6,8,9,12) |
| X | AU,B, 18280/70 (442954) (N.L. INDUSTRIES INC.) 3 February 1972 (03.02.72) See claims 1,4,11,12, Examples I, VI,VII,XIII and pp.16-19 | (1,4,5,9,10) |
| X,P | AU,A, 44989/89 (WIMERA INDUSTRIAL MINERALS PTY LTD) 14 May 1990 (14.05.90) See claims 1,3-5 ,8,11,12,20,21 and abstract | (1,3,4,10,11,13) |
| A | CH,A, 346030 (SOCIETE D'ELECTRO-CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE, PARIS) 15 June 1960 (15.06.60) See p.2 lines 70-96 | (1,10-12,16) |

(continued)

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

4 June 1991 (04.06.91)

Date of Mailing of this International Search Report

19 June 1991

International Searching Authority

Australian Patent Office

Signature of Authorized Officer

R. Howe

ROGER HOWE

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| | | |
|---|---|-------------|
| A | FR,A, 1066777 (TITAN COMPANY, INC.) 9 June 1954 (09.06.54) See claim 1 | (1,4,9,10) |
| A | GB,A, 251527 (A.W. GREGORY) 6 May 1926 (06.05.26) See claim 1 and p.1 lines 37-55 | (1,4,9,10) |
| A | Patents Abstracts of Japan, C-76, page 675, JP,A, 51-126316 (MITSUBISHI KASEI KOGYO K.K.) 4 November 1976 (04.11.76) | (1) |
| A | Derwent Soviet Inventions Illustrated, Section I Chemical, Issued 5 July 1973 (05.07.73), Metallurgy, p.15, SU 353 992 (PETRUNKO et al) May 1973 (00.05.73) | (1,4,9,10) |
| A | AU,A, 11196/70 (ISHIHARA SANGYO KAISHA LTD) 2 September 1971 (02.09.71) See claims 1,12,14,16 | (1,4,9) |
| A | AU,A, 183 20/70 (BRITISH TITAN PRODUCTS COMPANY LIMITED) 3 February 1972 (03.02.72) See claim 1 | (1,4, 9,12) |

V. [] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [] Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
2. [] Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. [] Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. [] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. [] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. [] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. [] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. [] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest.

- [] The additional search fees were accompanied by applicant's protest.
[] No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 91/00069

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | Patent Family Members | | | |
|--|----------|-----------------------|---------|----|---------|
| SU | 174363 | | | | |
| AU | 44989/89 | CA | 2001371 | WO | 9004656 |
| | | | | ZA | 8908010 |
| CH | 346030 | | | | |
| FR | 1066777 | | | | |
| GB | 251527 | | | | |
| JP | 51126316 | | | | |
| SU | 353992 | | | | |
| AU | 11196/70 | | | | |
| AU | 18320/70 | | | | |
| AU | 18280/70 | BE | 754202 | CA | 922520 |
| | | FR | 2053349 | NL | 7011285 |
| | | | | DE | 2038172 |
| | | | | US | 3647414 |