

# Procedures for Treating Ferrous Titanium Raw Materials

Eberhard Gock, Volker Vogt, and Marcela Achimovičová

**Abstract**—The subject of the invention is a new reaction mechanism, during which natural ferrous titanium minerals can be dissolved using dilute sulfuric acid (40%) at 50°C in the presence of hydrogen in statu nascendi. In the new process, titanium raw materials are milled with a metal additive that is less noble than hydrogen in order to generate briquettes of the highest bulk density. The atomic hydrogen that develops at the contact surfaces when adding diluted sulfuric acid, leads to a partial reduction of quadrivalent to trivalent titanium, thereby initiating a spontaneous and almost complete dissolution at 50°C and ambient pressure. After the separation of the iron by means of crystallization, it is possible to extract a TiO<sub>2</sub> concentrate as raw material for the production of titanium alloys.

**Index Terms**—Dissolution, Metal additive, Milling, Titanium raw materials.

## I. INTRODUCTION

There are a large number of commercial and proposed processes for extracting TiO<sub>2</sub> concentrates from ferrous titanium minerals as a raw material for the production of pigments. These processes consist of a combination of thermal treatment, leaching, and physical separation stages [1]-[22]. The iron is converted into soluble Fe<sup>2+</sup> or elementary iron by means of reduction at high temperatures, followed by acid leaching for the production of synthetic TiO<sub>2</sub> concentrates.

So far, there is no process technology for direct leaching of ferrous titanium minerals with mineral acids at normal pT conditions for the dissolution of titanium and iron with the objective of generating a TiO<sub>2</sub> concentrate by means of hydrolysis. If an ilmenite concentrate that has been produced by means of conventional processing methods, such as density sorting, magnetic separation, or electrostatic sorting, is subjected to a 60 min leaching with 40% H<sub>2</sub>SO<sub>4</sub> at 95°C, the titanium recovery is no more than 0.05% max. and the iron recovery 0.3%. This study introduces a new method that allows the dissolution of ferrous titanium minerals, especially ilmenite, with diluted mineral acid at temperatures below 100°C and to produce high percentage TiO<sub>2</sub> concentrates after the separation of the iron [23].

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## II. MATERIALS AND METHODS

Ilmenite concentrate with a grain size of 100% < 0.6 mm was used as input material with following chemical analysis: 45.6% TiO<sub>2</sub> (30.02% Ti), 34.43% Fe, 0.76% Si, 0.42% Al, 0.016% Cr, <50 ppm Th, <50 ppm U, 7 ppm Zr and <5 ppm P. Apart from ilmenite (FeTiO<sub>3</sub>), the X-ray diffraction analysis (XRD) also showed hematite (Fe<sub>2</sub>O<sub>3</sub>) and quartz (SiO<sub>2</sub>).

An industrial eccentric vibratory mill, type ESM-656 0.5 ks (Siebtechnik GmbH, Germany), equipped with a satellite milling container was used for the milling. The kinematic analysis as well as the mechanical model of the eccentric vibratory mill can be found in numerous publications [24]-[27]. The following constant conditions were applied: satellite containers 5 l, degree of milling media filling 80%, grinding media shape and size 30 mm steel balls, amplitude 20 mm, frequency 960 min<sup>-1</sup>. Mixing ratio ilmenite/aluminum powder = 19:1, activation time 15-180 min, 100-600 g/charge, argon atmosphere.

For the leaching tests, a 1 l beaker was used as open agitator vessel with magnetic stirrer. Sulphuric acid was used as a leaching agent. The leaching temperature was controlled via a thermostated heating plate. Samples were taken at defined intervals. The sampled suspensions were filtered and analyzed by means of inductively coupled plasma spectrometry (ICP-OES). The solutions were collected for crystallization and hydrolysis. The following leach parameters were analyzed: 30-60% H<sub>2</sub>SO<sub>4</sub>, solids content 150-300 g.l<sup>-1</sup>, leaching time: 5-60 min, start temperature 50°C.

A laser granulometer (Sympatec GmbH, Germany) was available for the particle size analysis.

The agglomerates were detected by means of a scanning electron microscope (SEM).

## III. RESULTS AND DISCUSSION

### A. Reaction Mechanisms during Ultrafine Milling

If a commercially available ilmenite concentrate is finely ground in a vibratory mill, which primarily applies impact stress, together with aluminum powder, there are two stages of stress: The stage of ultrafine milling and the stage of mechanical activation characterized by agglomeration [28]. A reproducible measure for the mechanical activation can be obtained by means of X-ray diffraction analysis. Lattice plane (104) was selected as the suitable lattice plane for ilmenite (see Fig.1).

The ratio of the X-ray microstructure intensities of the raw material (I<sub>0</sub>) to the X-ray microstructure intensities after a defined milling stress (I) yields a specific, characteristic value I/I<sub>0</sub>, which describes a specific active state of the milled material and the specific reaction-kinetic properties under defined conditions.

For example, at an  $I/I_0$  at lattice plane (104) of ilmenite, which was agglomerated in a mixture with 5 wt% Al, and with the use of 40%  $H_2SO_4$ , an extensive solubility of titanium is to be expected after 60 min. At  $I/I_0=1$  the solubility of titanium is only 0.05%.

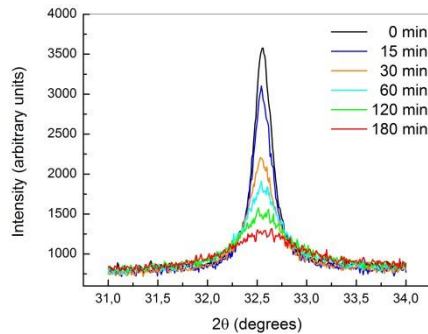


Fig.1. XRD measurements at the lattice plane (104) of ilmenite, which was agglomerated in a mixture of 5 wt% Al at 15, 30, 60, 120, and 180 min of activation.

Therefore, for the here significant agglomeration or briquetting during ultrafine milling, the X-ray diffraction coefficient  $I/I_0$  is available as a measurable value, which allows a quantification of the dissolution of titanium from the ferrous titanium mineral of ilmenite (Fig.2).

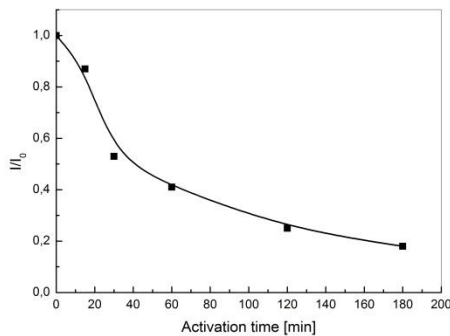


Fig. 2. Degree of activation  $I/I_0$  of a mixture of ilmenite and 5 wt% Al in dependence on the activation time.

Fig.3 shows the measured grain size distribution of the unmilled ilmenite and the activated ilmenite-aluminum mixtures. The milling with 5% aluminum powder causes strong agglomeration even after only 15 min of activation. The SEM image in Fig.4 shows the formed agglomerates.

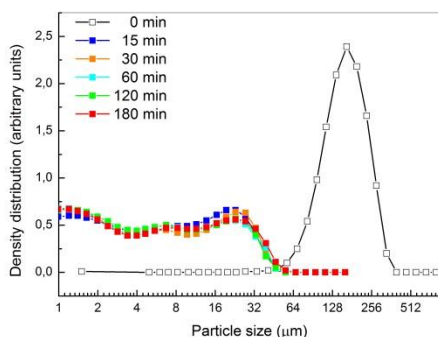


Fig.3. Grain size distributions of ilmenite-aluminum mixtures (5 wt% Al).

The XRD analysis of ilmenite-aluminum agglomerates proves that, apart from ilmenite and aluminum, no new phase

develops during the milling process. During the investigations on the high-energy mechanical activation of ilmenite in the presence of aluminum powder, solid state reactions were determined under the formation of  $Al_2O_3$ ,  $TiO$ ,  $Fe_2Ti$  and  $Fe$  [29].

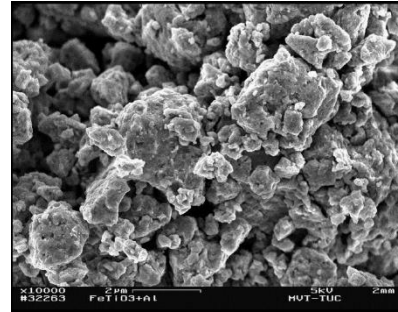


Fig.4. SEM picture of formed ilmenite-aluminum agglomerates [23].

### B. Parameter Studies on Open Leaching

During the leaching of activated ilmenite in the presence of iron powder it was determined that first-stage  $Fe^{3+}$  is reduced to  $Fe^{2+}$  and  $Ti^{4+}$  is not reduced [30]. In this study the reduction to  $Ti^{3+}$  leads to deeply violet solutions, even at a small partial reduction. According to Gmelin a reducing solution that contains 1% of  $Ti^{3+}$  turns deep black [31].

Fig.5 shows that the max. Ti-recovery of pure activated ilmenite reaches 23%. Activated ilmenite-aluminum mixture shows a 53% Ti dissolution after only 15 min of activation. The necessary agglomerates during milling already appear after 15 min of activation. The contact pressure caused by the impact stress on the agglomerates during the second stage of ultrafine milling lead to structures similar to briquettes. If diluted  $H_2SO_4$  is added to the ilmenite-aluminum mixtures, changed with this kind of stress, the highly reactive atomic hydrogen (in statu nascendi) emerging at the contact areas immediately reacts with the ilmenite, causing a partial reduction of the quadrivalent titanium to trivalent titanium, thereby generating a  $Ti^{3+}/Ti^{4+}$  solution.

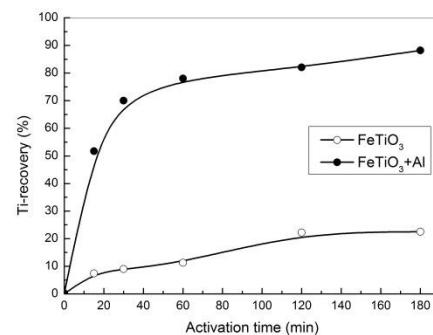


Fig.5. Influence of the activation time on the titanium extraction when using pure  $FeTiO_3$  and mixtures of ilmenite with 5% Al; leaching at a start temperature of  $50^\circ C$ .

Iron in ilmenite is bivalent, so that only a small trivalent part, oxidized under the influence of decomposition, has to be reduced [23].

Investigations on the influence of the initial acid concentration on the dissolution of an ilmenite-aluminum mixture ( $150 g.l^{-1}$ ) milled for 60 min, with the use of 30, 40, 50, or 60% sulphuric acid, show a maximum Ti-recovery of 79%

after a leaching time of 60 min and the use of 40% acid, corresponding to a solids/acid ratio of 1:3.3. With the increase of the initial acid concentration to 50%, corresponding to a ratio of 1:4.3 dissolved  $Ti^{4+}$  is partially hydrolyzed and the Ti-recovery decreases to 42%. For technical scale, the ratio of ilmenite to acid should be < 1:4. An excessively high amount of acid would complicate the hydrolytic conditions.

The amount of milling material per charge determines the milling result. Fig.6 shows the extraction of Ti in dependence on the milling material mass at a milling time of 60 minutes. Up to a milling material mass of 200 g/charge, the Ti-recovery during leaching is approx. 78%. With a further increase to 300 g/charge the Ti-recovery decreases by approx. 10% to 69%. At 600 g/charge, the result is still unexpectedly high with a Ti-recovery of 56%. Without milling the Ti-recovery is 0.3%.

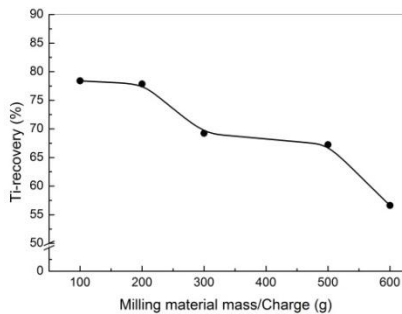


Fig.6. Influence of the milling material mass/charge on the titanium extraction after an activation time of 60 min and a solids content of 150 g.l<sup>-1</sup>, start at 50°C.

A check of the solids concentration per liter showed that the optimum solids concentration was 150 g.l<sup>-1</sup> (Fig.7). For technical processes, at least 300 g.l<sup>-1</sup> must be feasible.

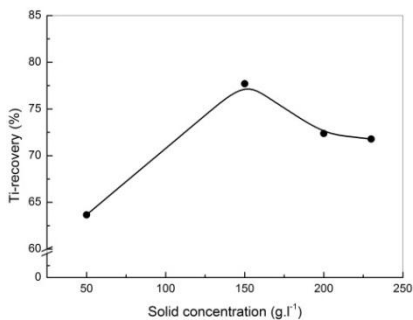
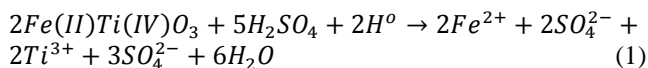


Fig.7. Influence of the solids concentration of ilmenite-aluminum mixtures (5 wt%) on the titanium extraction after 60 min of activation (200 g/charge), start temperature 50°C.

The leaching time was varied in a range between 5 to 60 mins. Fig. 8 shows that the leaching of ilmenite-aluminum mixtures happens rapidly at 50°C already. After no more than 5 min of leaching, the Ti-recovery is at 70 %. After 60 min of leaching the ilmenite dissolution is almost 80%.

The summation equation (1) of the conversion of ilmenite with diluted H<sub>2</sub>SO<sub>4</sub> in the presence of hydrogen in statu nascendi is [23]:



In an open agitator vessel ilmenite is largely dissolved at a

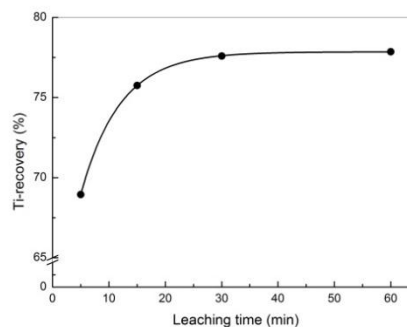


Fig.8. Influence of the leaching time on the titanium extraction, start temperature 50°C.

temperature of 50°C, since the strong bond in the briquetted mixture follows the shrinking core model [32]. Because of the violet color of  $Ti^{3+}$  the solution appears to be deep violet to black. Iron and aluminum as accompanying metals can be crystallized as a sulphate mixture by decreasing the temperature to <15°C. The TiO<sub>2</sub> can be won conventionally by means of hydrolysis. During calcination, Ti(OH)<sub>3</sub> as a by-product during hydrolysis, oxidizes to TiO<sub>2</sub> after the precipitation.

The utilization of atomic hydrogen can be proved by using a conclusion by analogy: aluminum powder is retroactively added to agglomerated ferrous ilmenite that had been activated in a vibratory mill, and the corresponding mixture is then exposed to a mineral acid. The hydrogen, emerging at the free aluminum grains, which have no contact with the ilmenite for taking up atomic hydrogen in the surface, spontaneously converts into the molecular form, so that the reducing effect on the titanium component is of subordinate importance due to the low solubility of molecular hydrogen in water and a significant dissolution of ferrous titanium minerals under normal pT conditions is not possible.

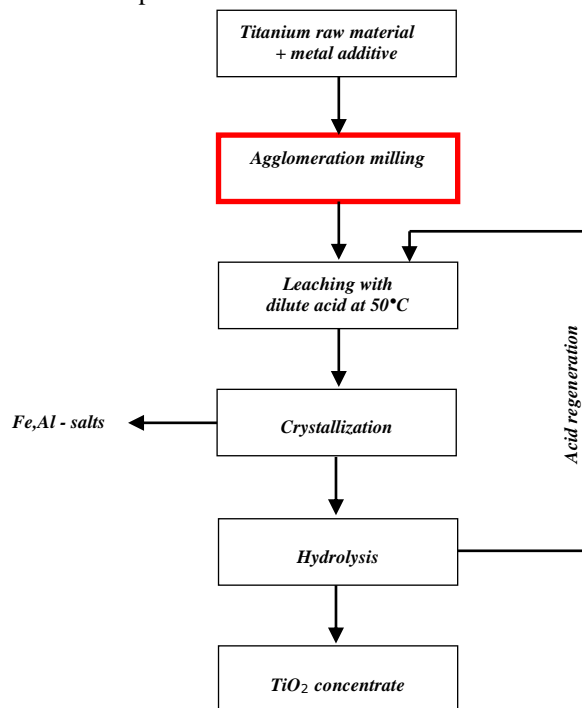


Fig.9. Proposed process for the production of synthetic TiO<sub>2</sub>.

The proposed process for the production of synthetic TiO<sub>2</sub> concentrate as shown in Fig.9 is derived from the above described reaction kinetic investigations.

#### IV. CONCLUSION

This study determined the reaction mechanism during the dissolution of ilmenite by means of a reduction with atomic hydrogen on a laboratory scale. An optimization for the commercial scale of the process has not been performed. It was proven that a process stage optimization from 7 to 5 stages, compared to the conventional sulphate process, is feasible.

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