

Article

# Sulphuric Acid Digestion of Anatase Concentrate

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**Abstract:** The processing of anatase ores by sulphuric acid digestion is well known for its low titanium dissolution yields, which makes the process economically and technically unfeasible. Anatase is considered much less reactive than other forms of titanium such as ilmenite and rutile. Generally, to enhance its dissolution, thermal processes along with acid and/or alkaline leaching processes are necessary. Studies of direct sulphuric acid digestion are few and the reported yields of titanium dissolution are <48%. This study investigated the main parameters of sulphuric digestion of anatase such as temperature, anatase:acid ratio, and time of reaction. Dissolution of titanium of around 86% were obtained at relatively mild conditions such as, temperature at 220 °C, grain size of 62 µm, an anatase:sulphuric acid ratio of 1:2, and 4 h of reaction. A comprehensive characterization of the resulting material indicated a content of 56.5% of TiO<sub>2</sub> and 15% iron oxide—the main impurity. It also contained silica, aluminum, phosphorus, calcium, and rare earth elements (REE) in concentrations that varied from 1.61% to 6.01%.

**Keywords:** anatase; titanium; sulphation; phosphorus

## 1. Introduction

There are many known titanium minerals that are classified into five groups: rutile (TiO<sub>2</sub>), ilmenite (FeO·TiO<sub>2</sub>), perovskite (CaO·TiO<sub>2</sub>), pyrochlore (Na,Ca,...)(Nb,Ti)<sub>2</sub>O<sub>6</sub>(F,OH), and sphene CaTiSiO<sub>4</sub>·(O,OH,F). The rutile-type minerals in the first group (anatase TiO<sub>2</sub>, brookite TiO<sub>2</sub>, leukocene TiO<sub>2</sub>·nH<sub>2</sub>O, etc.) can be found together due to the proximity of the titanium ionic radii making it possible to substitute isomorphically with other metals [1]. Some elements can substitute titanium (Ti<sup>4+</sup>) in the anatase lattice depending on the temperature and pressure of formation; iron is an example. The substitution mechanism is controlled by the ionic charge and radius, resulting in a solid solution [2]. During the hydrometallurgical process, iron generally dissolves, because the sulphuric digestion produces soluble iron sulphate. The presence of ferric ions in the liquor can be associated with the existence of dissolved oxygen in the system. Fe<sup>3+</sup> will form Fe(OH)<sub>3</sub> and, if not eliminated from the liquor, can cause contamination of the final product. However, iron can be removed using solvent extraction, anion exchange resins, and complexation with ethylenediaminetetraacetic acid (EDTA) during hydrolysis [3,4]. Other impurities in the raw material such as Zr and Nb can also influence the purity of the final product.

For the production of pure titanium dioxide, as well as for metallic titanium, the ilmenite and rutile are the main Ti source. However, with the increasing demand for titanium, the deposits of these minerals are gradually depleting and anatase has become of great interest as a possible option to replace them [5]. The global reserves of anatase are abundant, and Brazil is the country with the largest anatase reserve (440 Mt) containing an average of 17.7 wt% TiO<sub>2</sub> [6,7]. In the State of Minas Gerais, 200 Mt of anatase containing 12% to 15% of TiO<sub>2</sub>, is a residue of the phosphate exploration, which is stored in piles. The



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residue remains without defined use because a commercial process to produce highly pure  $\text{TiO}_2$  that has proved to be technically and economically feasible has not been developed.

Considered as a “strategic mineral”, the search for potential sources of titanium minerals is paramount. However, many difficulties exist in the use of anatase as a raw material, one is its low chemical reactivity, which leads to significantly low sulphation efficiency and the other is the existence of a complex mineralogy assemblage that directly influences the downstream purification steps. In addition, it is not possible to obtain an anatase concentrate suitable to feed conventional processes—chloride or sulphate—by using only physical beneficiation methods. Moreover, anatase is a difficult mineral to leach [2,5,8]. For these reasons, although there are several anatase deposits in Brazil, they have not been exploited for titanium production [9].

The great majority of the studies about the production of high-grade  $\text{TiO}_2$  focus on ilmenite, which is far more reactive and consequently, more easily solubilized than anatase. Other forms of  $\text{TiO}_2$  such as rutile and leucosene, whose acid digestion is also difficult, need very fine grains and thermal reduction to enable the dissolution of Ti. Because of the low reactivity of anatase, studies since 1980 have focused on the upgrade of anatase concentrate in order to eliminate the impurities and raise the content of  $\text{TiO}_2$ . Different pyrometallurgical and/or hydrometallurgical treatments were extensively investigated, mainly alkaline or reductive roasting followed by leaching, but direct sulphuric digestion was scarcely evaluated [2,8,10,11]. However, the process still accounts for 40% of the total  $\text{TiO}_2$  pigment produced in the world [12,13]. The main advantages of the sulphate process are the low capital costs and flexibility, as the process allows the use of low grade titanium raw materials, such as the residues from the phosphate exploration.

Sulphuric acid digestion is the first stage of the sulphate process and consists of the digestion of the raw material (fine grain size 90% < 44  $\mu\text{m}$ ) with concentrated sulphuric acid (80–98%), at temperatures between 170 and 220 °C, and reaction times that vary from 2 to 6 h. After the reaction time, the solid is leached with water to promote the solubilization of sulphates and to obtain a liquor containing the metal of interest [10,14,15]. In the case of titanium, the raw material is converted to solid titanyl sulphate ( $\text{TiOSO}_4$ ), which is soluble in water and can be leached into a titanyl sulphate rich liquor. That is followed by hydrolysis to produce hydrated titania.

The dissolution kinetics of titanium in an acid digestion is linked to various factors, such as acid concentration, particle size, reaction time, and solid-liquid ratio. In a sulphuric digestion, Ti dissolution increases when the concentration of sulphuric acid is higher than 3M. The amount of other elements that are dissolved from the raw material is dependent on this factor as well. Moreover, the density and viscosity depend on sulphuric acid concentration and can result in unnecessary acid consumption, low fluidity, and high cost [16–19].

According to Jablonski and Tylutka (2016) [17], the maximum temperature reached in the process and the time spent to reach its maximum are dependent on the acid concentration. At low concentrations, the reaction is unstable, which may indicate incomplete sulphation of the material. In order to implement the sulphate process, the ideal is that the minerals of interest have high solubility in sulphuric acid and exothermicity that allows the reaction to be sustained after reaching the ignition temperature. However, this is not always the case in all titanium minerals and anatase is an example [15]. Particle size influences the leaching rate, such that generally small particles improve the dissolution kinetics, but this effect is not significant to particles <105  $\mu\text{m}$  [18].

Table 1 provides a literature review of studies using anatase as a feedstock.

However, up to now, there is no definition of one technological route, economically and technically viable, for the production of pure  $\text{TiO}_2$  from anatase ore. The present study investigated the chemical dissolution of an anatase concentrate containing 56.5% of  $\text{TiO}_2$  by means of sulphation in order to present a feasible technical alternative to produce high grade  $\text{TiO}_2$  using residues from the mining industry.

**Table 1.** Examples of different processes to produce pure TiO<sub>2</sub> from anatase ore concentrate.

Authors	Anatase Ore Concentrate— TiO <sub>2</sub> (%)	Processes
Chao and Senkler (1991) [20]	74.5	Upgrade: chloride leaching, alkaline leaching, chloride leaching
Chao et al. (1993) [21]	62.9	Upgrade: a reducing roasting, magnetic separation, pressure chloride leaching
Freitas et al. (2007) [22]	53.8	Upgrade: calcination, reduction in H <sub>2</sub> , magnetic separation, chloride leaching
Freitas and Gracioso (1985) [23]	70.0	Chloride leaching, alkaline digestion, sulphuric digestion, hydrolysis- precipitation
Jha and Tathavadkar (2005) [24]	57.8	Alkaline digestion, leaching with water,
Patent: Mineração Vale do Paranaíba (1980) [25]	78.1	Upgrade: Acid digestion under pressure, chloride leaching, magnetic separation
Paixão and Mendonça (1979) [26]	75.6	Upgrade: roasting, magnetic separation, HCl chloride leaching, NaOH neutralization
Smith Jr and Castro Sheldon (2007) [27]	52.9	Upgrade: leaching in autoclave with H <sub>2</sub> SO <sub>4</sub> and FeSO <sub>4</sub> , drying with NaCl addition, calcination, chloride leaching
Trindade e Teixeira (1988) [11]	76.5	Upgrade: chloride leaching in 4 stages

## 2. Materials and Experimental Procedure

### 2.1. Material

A Brazilian anatase ore, physically concentrated and containing around 57% TiO<sub>2</sub>, was used in this investigation. The grain size was 99.3% < 62 µm. This pre-determinate grain size was obtained by milling all of the material in a bar mill and sieving using a 62 µm sieve.

### 2.2. Chemical and Mineralogical Characterization

The Brazilian anatase concentrate and the residues from the processed samples were chemically characterized by Wavelength-dispersive X-ray spectroscopy (WDS) model Primus II, by Rigaku, manufactured in Japan, with a rhodium tube, vacuum system, Lithium Fluoride crystal, Pentaerythritol, RX25, Ge and RX35 crystals, scintillation detector, and gas flow proportional counters.

The mineralogical characterization was carried out using a FEI Quanta 200 field emission gun (FEG) Scanning Electron Microscope (SEM) equipped with a secondary electron detector, backscattered electron detector, transmitted electron detector (STEM), integrated detector Pegasus: EDS (Energy-dispersive X-ray spectroscopy), and EBSD (Electron backscatter diffraction), operating at voltages between 200 V and 30 kV, with a beam current greater than 100 nA, a resolution of 1.6 nm at 30 kV in high vacuum and ESEM<sup>TM</sup> mode and of 3.5 nm at 3 kV at low vacuum, a focal length of 3 mm to 99 mm, and 12× magnification (at the longest working distance) at 1,000,000× at high and low vacuum. X-ray diffraction was also employed and the analysis was conducted using Rigaku equipment, D/Max Ultima Plus model, Japan, using Cu (Kα) radiation with a wavelength of 1.5418 Å, tension of 40 kV and current of 30 mA. The samples were prepared by the powder method and the analysis was made in a 2θ angle range from 4° to 80°, with a scan step size of 0.02° s<sup>-1</sup>. The qualitative analysis of the mineral phases was performed by comparing the diffractograms with crystallographic reference standards available in the JCPDS-ICDD database (Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data). The textural characterization of the mineralogy was achieved using scanning electron microscopy (SEM), performed on an FEI Quanta 200 field emission gun (FEG) scanning electron microscope with energy-dispersive X-ray spectrometry (EDS) and back-scatter electron imaging capabilities.

### 2.3. Sulphuric Digestion

The sulphuric digestion process was carried out with sulphuric acid (98%), at temperatures of 190 °C, 200 °C, 210 °C, and 220 °C, anatase concentrate:sulphuric acid ratios of 1:1.3 and 1:2 (*w/w*), and times of 3, 4, and 5 h. The concentrate and sulphuric acid were manually homogenized and heated according to previously determined conditions. After sulphuric digestion, the system was leached with Milli-Q water or dilute sulphuric acid at 70 °C. After leaching, the slurry was filtered under vacuum and the solid was washed with a volume of Milli-Q water, dried, and sent to be analyzed. All of the experiments were performed in duplicate. The metallurgical recovery was calculated using Equation (1):

$$R_m = \left[ 1 - \left( \frac{m_r \times c_r}{m_c \times c_c} \right) \right] \times 100 \quad (1)$$

where  $m_r$  is the mass of residue,  $c_r$  is the  $\text{TiO}_2$  concentration in the residue,  $m_c$  is the mass of concentrate and  $c_c$  is the  $\text{TiO}_2$  concentration in the concentrate.

## 3. Results and Discussion

### 3.1. Chemical and Mineralogical Characterization of the Anatase Concentrate

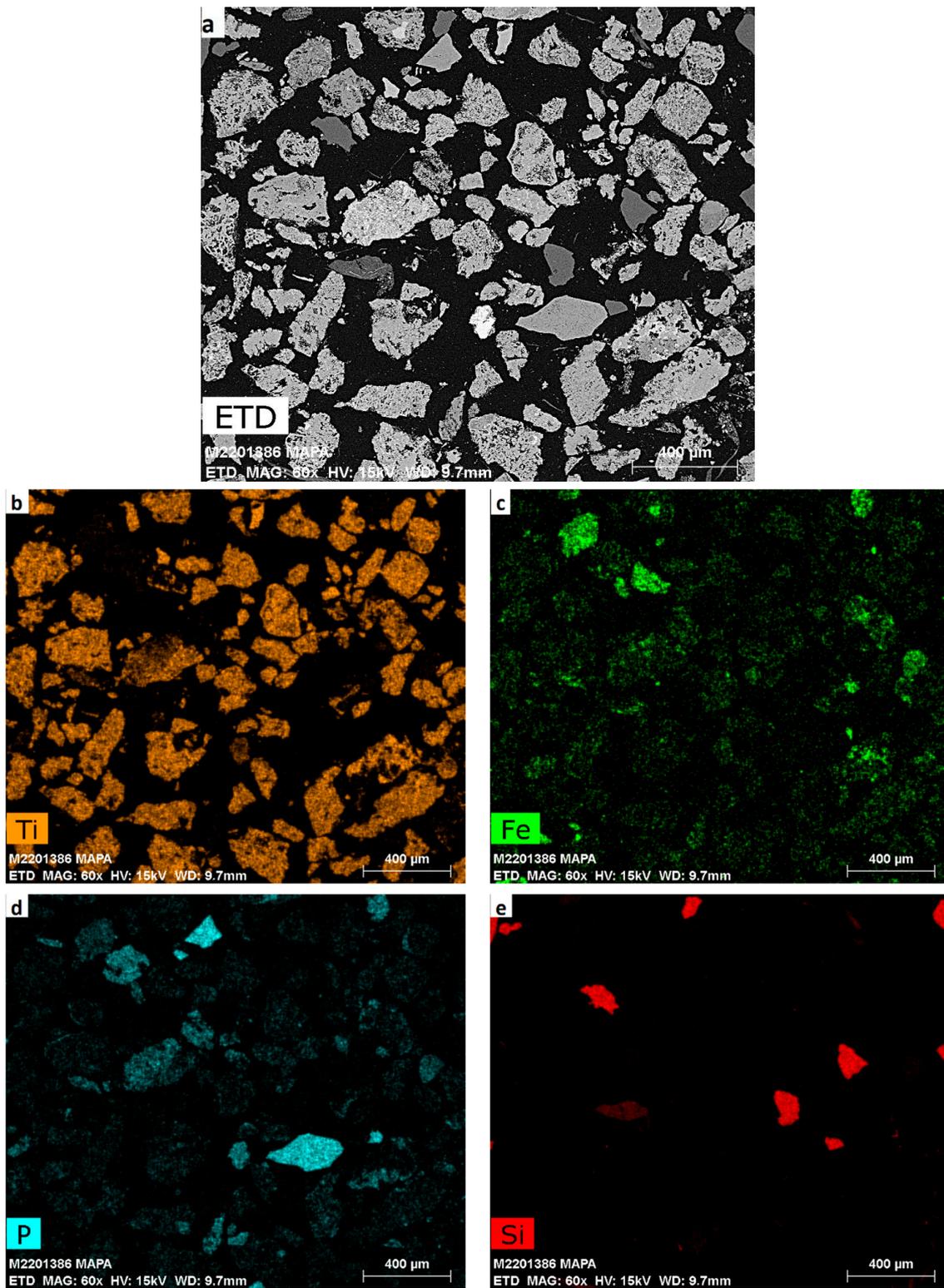
The chemical analysis (Table 2) indicated that the anatase ore concentrate had a content of 56.5% of  $\text{TiO}_2$  and the main impurity was iron oxide, at 15%. The concentrate also had silica, aluminum, phosphorus, calcium, and rare earth elements (REE), whose contents varied from 1.61% to 6.01%. The concentrate also contained other impurities in smaller proportions such as  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ .

**Table 2.** Chemical characterization of the anatase concentrate.

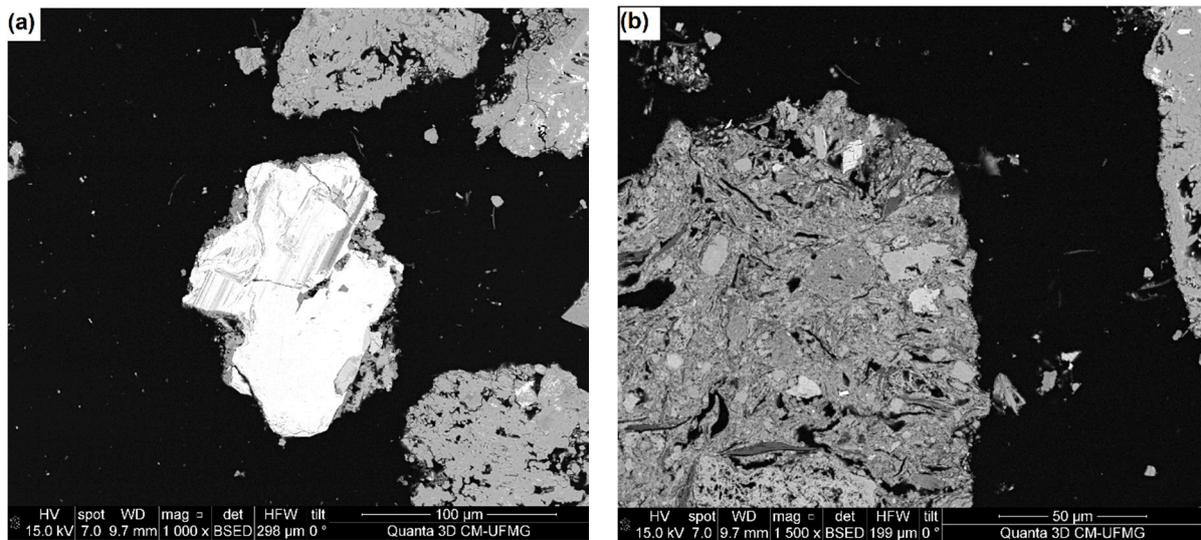
Elements	Anatase Concentrate (%)
$\text{TiO}_2$	56.5
$\text{Fe}_2\text{O}_3$	15.0
$\text{P}_2\text{O}_5$	4.11
$\text{SiO}_2$	6.01
$\text{Al}_2\text{O}_3$	5.34
CaO	1.61
$\text{ZrO}_2$	0.59
$\text{Nb}_2\text{O}_5$	0.62
REE	2.19

The material was also analyzed by SEM-EDS, and Figure 1a presents the general morphology of the sample where we can see the heterogeneity of mineral phases, the chemical composition, as well as a large dispersion in particle size. The SEM image also shows particles of a few hundred nanometers aggregated to micrometric particles of phyllosilicates. Figure 1b–e shows the main elements present in the concentrate.

Figure 1b–e shows the expressive presence of Ti, P, Fe, and Si. These minor elements can replace Ti in the crystal lattice depending, in part, on the ionic charge and radius of the element. Those cations with a higher charge and/or a smaller radius than  $\text{Ti}^{4+}$  ( $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mo}^{4+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Sb}^{3+}$ ) are preferentially accepted. These impurity elements may also be distributed in several different minerals with significant intergrowths between them. In this case, although present in smaller amounts, Nb and Zr were found as inclusions in  $\text{TiO}_2$  grains substituting titanium in the lattices of the anatase crystal (Figure 2). The presence of these metals prevents the obtaining of products with a high  $\text{TiO}_2$  content [2], making it difficult to achieve acceptable impurity levels.

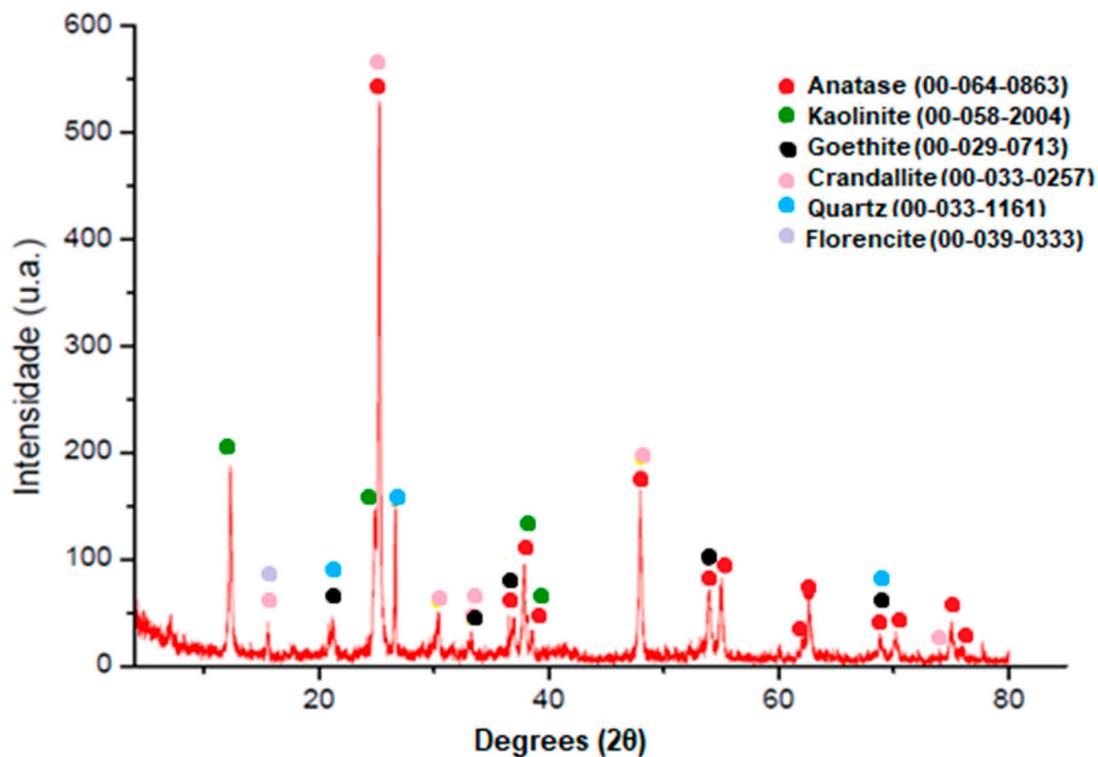


**Figure 1.** (a) General map of the elements present in the anatase concentrated by SEM-EDS (SE-SEM, 60× magnification). Backscattered electron image from SEM showing representative particles of anatase concentrate and X Ray element maps for (b) Titanium; (c) Iron; (d) Phosphorus; and (e) Silicon.



**Figure 2.** (a) Calzirtite grain surrounded by Anatase grain containing Zr, Ti, and Ca (SE-SEM, 1000× magnification); (b) Crandalite grain with inclusion of ilmenite, ilmenorutile, hematite and kaolinite (SE-SEM, 1500× magnification).

The X-ray diffraction diagram (Figure 3) indicates the mineralogical phases of the anatase concentrate, making it possible to predict the reactivity of each phase during the acid digestion process. The peak of highest intensity refers to anatase ( $\text{TiO}_2$ ). Goethite ( $\text{FeOOH}$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), quartz ( $\text{SiO}_2$ ), crandallite ( $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ), and florencite ( $\text{NdAl}_3(\text{PO}_4)_2(\text{OH})_6$ ) were also identified. In this material, crandallite and florencite make a solid solution.

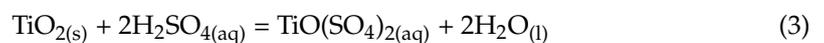
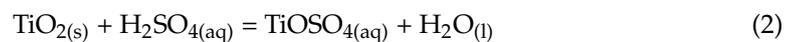


**Figure 3.** X-ray diffraction diagram of the anatase ore concentrate.

As impurities are present in anatase grains as inclusions, it is difficult to obtain a high purity concentrate using only physical processing, as the tightly intergrown crystals of minerals may affect liberation [28]. SEM analysis (Figure 1) confirmed these intergrown crystals of minerals, since it was observed that several elements are present in the same grain.

### 3.2. Sulphuric Acid Digestion

Generally, sulphuric acid digestion consists of heating the ore along with concentrated sulphuric acid (80–98%) at temperatures of up to 300 °C for periods of 2 to 6 h. The process is a pre-treatment to produce metal sulphates soluble in water. The dissolution in water produces a liquor containing various metals, not only the one of interest. This technique aims to transform a difficult-to-leach metal oxide to a more readily leachable metal sulphate [10,14,15,29–31]. The sulphuric digestion of titanium ore followed by leaching with water, produces a liquor rich in soluble titanyl sulphate ( $\text{TiOSO}_4$ ), however, it also contains some impurities. The process can be described according to the following reactions.



According to Aguiar (2021) [32], during dissolution, the titanium usually presents an oxidation number of +4 and the metal is commonly linked to oxygen, forming  $\text{TiO}^{2+}$ . The interaction of this species with  $\text{SO}_4^{2-}$  results in  $\text{TiOSO}_4$  (Equation (4)), which, in turn can lead to the formation of  $\text{TiO}(\text{SO}_4)_2$  (Equation (5)).

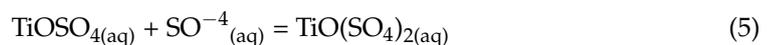
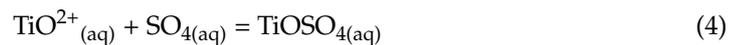
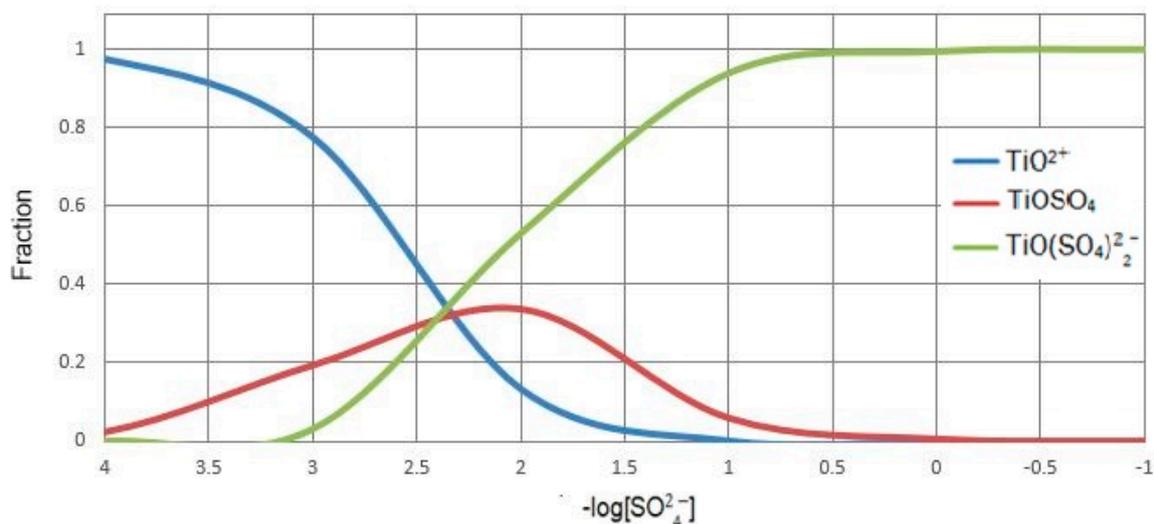


Figure 4 shows the distribution diagram for titanium species in sulphuric medium considering  $\text{TiO}^{2+}$ ,  $\text{TiOSO}_4$ , and  $\text{TiO}(\text{SO}_4)_2$ .



**Figure 4.** Distribution diagram for Ti species in sulphuric medium; [titanium total concentration = 1 mol/L,  $K_1 = 10^{-2.396}$ ,  $K_2 = 10^{-2.197}$ ].

The average concentration of  $\text{SO}_4^{2-}$  in the liquor after leaching reported in the literature is 2 M [2,33]. In Figure 4, at 2 M sulphate, the species present in the liquor is 100%  $\text{TiO}(\text{SO}_4)_2$ . However, Jablonski and Tylutka (2016) [17], Zhang et al., (2011) [34], and Freitas and Brocchi (1995) [15], among others, mention only the presence of  $\text{TiOSO}_4$  in titanium liquors and do not refer to the species  $\text{TiO}(\text{SO}_4)_2$ .

### 3.2.1. Effect of Temperature on Sulphuric Digestion of the Concentrate

Temperature is an important variable in sulphuric digestion as it accelerates the decomposition of the minerals and the conversion of the metals into soluble sulphates. Generally, the temperature of sulphuric digestion for the metallurgy of titanium varies from room temperature to 330 °C. Table 3 shows the TiO<sub>2</sub> content for the residues generated from sulphuric digestion followed by water leaching and the metallurgical recoveries calculated by Equation (1).

**Table 3.** Percentage of the main elements in the residues of the sulphuric digestion/leaching process (%) and metallurgical recoveries (%) for different temperatures.

T (°C)		TiO <sub>2</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	ZrO <sub>2</sub> (%)	Nb <sub>2</sub> O <sub>5</sub> (%)	Mass Reduction (%)
190	Residue	57.2 ± 1.2	8.14 ± 0.13	1.60 ± 0.08	0.83 ± 0.14	1.08 ± 0.03	68.9
	Metallurgical recovery	68.6	83.1	87.9	56.3	45.9	
200	Residue	50.9 ± 0.0	7.52 ± 0.42	2.59 ± 0.06	0.51 ± 0.04	0.95 ± 0.05	63.4
	Metallurgical recovery	67.0	81.6	76.9	68.6	43.4	
210	Residue	47.8 ± 0.6	8.24 ± 0.35	2.71 ± 0.06	0.63 ± 0.02	1.04 ± 0.02	70.9
	Metallurgical recovery	75.4	84.1	80.8	68.9	51.0	
220	Residue	35.8 ± 1.7	7.87 ± 0.17	4.40 ± 0.36	0.46 ± 0.07	0.66 ± 0.14	78.0
	Metallurgical recovery	86.0	88.4	76.5	82.9	76.4	

Experiments carried out in duplicate. Time of reaction: 4 h; solid:acid ratio: 1:2; leaching agent: Milli-Q water; solid:liquid ratio: 1:4; time of leaching: 2 h; temperature of leaching: 60 °C.

Table 3 shows the increase in metallurgical recovery from 67 to 86% with increasing temperature, as the heat favors the process. These results are promising, since the literature, although quite scarce, reports yields of sulphuric digestion of concentrates < 50% [15]. The titanium metallurgical recoveries increase with the temperature in the following order: 190 °C = 200 °C < 210 °C < 220 °C. When the temperatures are 190 °C and 200 °C, a small difference is observed between the metallurgical recoveries and the titanium extraction rates are close. A significant rise in metallurgical recovery was observed for the experiments at 220 °C. In contrast to the ilmenite ore, the reaction of anatase with sulphuric acid is not exothermic, which is one great disadvantage as it will be necessary to add heat during the entire reaction time to sustain the process [35]. The significant levels of TiO<sub>2</sub> in the residues compared to the anatase concentrate indicate that there was a significant mass reduction, which, in this case, was between 69 and 78% (Table 3). The increase in the contents of SiO<sub>2</sub>, K<sub>2</sub>O, SrO, and BaO indicate that sulphates that formed are insoluble or the mineral did not react with the acid and remained in the residue.

Regarding other chemical elements, such as Fe and P, their dissolution was considerably high, which will need a further process of purification. The metallurgical recovery of these elements ranges from 76.9 to 88.0%. Related to iron, the metallurgical recoveries are similar for the temperatures investigated, while for phosphorus, the recoveries are relatively higher at lower temperatures. Moreover, Zr and Nb were considerably dissolved, mainly at 220 °C, which is in disagreement with the literature [2], which reports poor dissolution of these elements in acid leach.

### 3.2.2. Effect of the Anatase Concentrate:Sulphuric Acid Ratio in the Digestion

The amount of acid necessary to convert the main minerals into soluble sulphate was calculated based on the stoichiometric of the chemical reaction between the anatase concentrate and the sulphuric acid. It took into account the content of the following elements present in the minerals: Ca, Ti, Fe, Al, Mn, V, Nb, and Zr. The stoichiometric is equivalent

to 1000 g of anatase concentrate for 1097 g of sulphuric acid, which implies an anatase concentrate:sulphuric acid ratio of 1:1.1. Bekker and Dutton (2004) [35] suggested the use of an anatase concentrate:sulphuric acid ratio equal to 1:1.3 (w/w) when investigating the dissolution of titanium. Therefore, in order to ensure an effective sulphation, the minimum amount of acid used was slightly above the stoichiometric one, which corresponds to the ratio 1:1.3 (w/w). Table 4 shows the relationship between the anatase concentrate:sulphuric acid ratio, the TiO<sub>2</sub> content in the residue, and the metallurgical recoveries.

**Table 4.** Percentage of the main elements in the residues and metallurgical recoveries to evaluate the influence of the anatase concentrate:sulphuric acid ratio in the sulphuric digestion.

Anatase:H <sub>2</sub> SO <sub>4</sub>		TiO <sub>2</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	ZrO <sub>2</sub> (%)	Nb <sub>2</sub> O <sub>5</sub> (%)	Mass Reduction (%)
1:1.3	Residue	51.9 ± 0.8	7.62 ± 0.89	2.32 ± 0.37	0.46 ± 0.05	1.00 ± 0.07	69.0
	Metallurgical recovery (%)	71.6	84.5	82.2	76.1	50.4	
1:2	Residue	35.8 ± 1.7	7.87 ± 0.17	4.40 ± 0.36	0.46 ± 0.07	0.66 ± 0.14	78.0
	Metallurgical recovery (%)	86.0	88.4	76.5	82.9	76.4	

Experiments carried out in duplicate. Time of reaction: 4 h; temperature: 220 °C; leaching agent: Milli-Q water; solid:liquid ratio: 1:4; time of leaching: 2 h; temperature: 60 °C.

According to Table 4, by increasing the anatase concentrate:sulphuric acid ratio from 1:1.3 to 1:2, the metallurgical recovery increased from 71.6% to 86.0% and the titanium contained in the residue decreased from 51.9% to 35.8%. For the 1:2 ratio, the free sulphuric acid concentration in the liquor was 1.8 M and the titanium concentration was approximately 35 g/L.

The greater amount of sulphuric acid in the 1:2 ratio favors the formation of all kinds of soluble sulphates, and consequently, the dissolution of a large part of the contaminants occurred, which ranged from 76.1% to 88.4%. The dissolution of niobium was the most affected by the increase of the concentrate:acid ratio, whose metallurgical recovery increased from 50.4% to 76.4%, which implies a higher concentration of niobium in the liquor. In a study carried out by Freitas and Brocchi (1995) [15], the authors used an anatase concentrate:acid ratio of 1:1.55 and the metallurgical recovery was only 48.4%. Bekker and Dutton (2004) [35] in a study of the digestion of steelmaking slags stated that the amount of sulphuric acid is the limiting factor for the occurrence of the reactions.

### 3.2.3. Effect of Time in Sulphuric Digestion

During digestion, it is important to ensure that the time is adequate for the effective sulphation of the titanium. Generally, 2 to 6 h are sufficient to promote the conversion of the anatase into soluble sulphate [15,29]. Table 5 shows the percentage of each element present in the residues of the digestion and metallurgical recoveries for different times.

According to Table 5, for 3 h of sulphuric digestion, the metallurgical recovery of TiO<sub>2</sub> was 82.3%, a value close to that using 4 h of digestion, 86.0%. Increasing the time of sulphuric digestion to 5h reduced the metallurgical recovery. Time does not seem to be a decisive variable when it comes to the dissolution of iron, phosphorus, and zirconium, since the metallurgical recoveries of these species, although high, 77.4% to 88.4%, remained stable. Niobium, in turn, showed a considerable increase in solubilization for the 4 h of digestion, reaching 76% of dissolution, while for the other times of digestion the metallurgical recoveries are close to 61%. The decrease in titanium extraction over time can be associated with the formation of a solid product layer, i.e., a ferric sulphate layer, which limits the progression of the reaction by blocking the diffusion of sulphuric acid towards the reaction front [14].

**Table 5.** Chemical characterization of the residues from the sulphuric digestion/leaching and the metallurgical recoveries for different reaction times.

Digestion Time (h)		TiO <sub>2</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	ZrO <sub>2</sub> (%)	Nb <sub>2</sub> O <sub>5</sub> (%)	Mass Reduction (%)
3	Residue	39.3 ± 1.3	8.72 ± 0.39	3.41 ± 0.17	0.52 ± 0.07	0.96 ± 0.09	87.3
	Metallurgical recovery (%)	82.3	85.2	78.9	77.4	60.3	
4	Residue	35.8 ± 1.7	7.87 ± 0.17	4.40 ± 0.36	0.46 ± 0.07	0.66 ± 0.14	78.0
	Metallurgical recovery (%)	86.0	88.4	76.5	82.9	76.4	
5	Residue	44.0 ± 0.6	7.43 ± 0.32	3.17 ± 0.08	0.44 ± 0.06	0.82 ± 0.05	72.0
	Metallurgical recovery (%)	78.2	86.1	78.4	79.2	62.7	

Experiments carried out in duplicate. Temperature: 220 °C; solid:acid ratio: 1:2; leaching agent: Milli-Q water; solid:liquid ratio: 1:4; time of leaching: 2 h; temperature: 60 °C.

### 3.2.4. Effect of Using Dilute Sulphuric Acid as a Leaching Agent

In addition to leaching using water, another alternative to dissolve the titanium sulphate after the sulphuric acid digestion, is to leach the material with dilute sulphuric acid. Therefore, H<sub>2</sub>SO<sub>4</sub> 5% was used as a leaching agent in an attempt to improve the process. Table 6 shows the comparison of the use of the two leaching agents.

**Table 6.** Chemical characterization of the residues from the sulphuric digestion/leaching and the metallurgical recoveries for different leaching agents.

Leaching Agent		TiO <sub>2</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	ZrO <sub>2</sub> (%)	Nb <sub>2</sub> O <sub>5</sub> (%)	Mass Reduction (%)
H <sub>2</sub> SO <sub>4</sub> 5%	Residue	40.7 ± 2.9	6.44 ± 0.52	3.54 ± 0.28	0.48 ± 0.09	0.87 ± 0.07	75.3
	Metallurgical recovery (%)	81.2	88.9	77.7	78.42	63.2	
Milli-Q water	Residue	35.8 ± 1.7	7.87 ± 0.17	4.40 ± 0.36	0.46 ± 0.07	0.66 ± 0.14	78.0
	Metallurgical recovery (%)	86.0	88.4	76.5	82.9	76.4	

Experiments carried out in duplicate. Time of reaction: 4 h; temperature: 220 °C; solid:acid ratio: 1:2; solid:liquid ratio: 1:4; time of leaching: 2 h; temperature: 60 °C.

In general, H<sub>2</sub>SO<sub>4</sub> is considered a suitable leaching agent, however, the results indicated that H<sub>2</sub>SO<sub>4</sub> 5% had the same efficiency as water. When water was used, the process efficiency was 86.0%, and for H<sub>2</sub>SO<sub>4</sub> the efficiency was 81.2%. Neither leaching agent is selective and the dissolution of other elements such as niobium, zirconium, and iron occurs in similar extension. Therefore, water is a better option to solubilize titanium after the sulphuric digestion.

The final solid residue after sulphuric digestion/leaching for the best test (86% metallurgical recovery) was analyzed by XRD. The identified phases were: anatase (TiO<sub>2</sub>), goethite (FeOOH), kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), and quartz (SiO<sub>2</sub>). The absence of crandallite (CaAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>5</sub>·H<sub>2</sub>O) and florencite (NdAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) indicates that they were effectively dissolved during the leaching and their contents in the residue were below the XRD detection limit.

## 4. Conclusions

Anatase is a non-reactive mineral, which makes digestion with sulphuric acid much more difficult than the digestion of other titanium minerals, such as ilmenite. This meant that for many years the processes that used anatase as a source of titanium were focused on the removal of the impurities (upgrade) and not on the digestion of the ore. However,

by applying the experimental conditions proposed in this investigation about 86% of the titanium was dissolved, showing that the process of sulphation was greatly enhanced. The optimal conditions are (i) digestion: anatase concentrate:sulphuric acid ratio of 1:2, a temperature of 220 °C, and a time of 4 h; (ii) leaching with water: solid:liquid ratio of 1:4, a time of 2 h, and a temperature of 60 °C. The main impurities, such as Fe, P, Zr, and Nb, were also dissolved from 76.5 to 88.4% and a further step for the purification of the liquor might be necessary. However, the viability of producing TiO<sub>2</sub> from anatase ores or even from anatase mining residues by sulphuric digestion can turn into reality as one of the issues—the low dissolution of Ti during sulphuric digestion—was solved. It is important to stress that titanium precipitation by hydrolyses and the purification of the precipitate is under continuing investigation in our laboratory.

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