# Extraction of Titanium from Low-Grade Ore with Different Leaching Agents in Autoclave

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**Abstract:** The progressive depletion of primary sources to obtain metals has led to the search for alternative sources for their recovery. In the particular case of titanium, titaniferous sands are a viable option for obtaining this metal. This paper presents the results of the dissolution of titanium from titaniferous sands of Buenos Aires province (Argentina) in a laboratory autoclave (450 mL of capacity). The operating parameters studied were as follows: different acids (HF, $H_2SO_4$ and mixtures of these acids); leaching agent concentration, 5–20% *v/v*; temperature, 75–150 °C; time, 30–180 min; solid–liquid ratio, 0.9–3.6% *w/v*; stirring speed, 110–550 rpm. The obtained results indicate that the increase in the leaching agent(s) concentration, temperature and time of contact with the acid mixtures have a marked effect on the dissolution reaction of titanium. Optimal conditions to achieve 89% extraction of titanium were obtained by leaching at 123 °C, 330 rpm, 80 min and 1.8% *w/v* with a mixture of 15% HF (*v/v*) and 10% $H_2SO_4$ (*v/v*).

## 1. Introduction

Titanium is the ninth most abundant element and constitutes approximately 0.6% of the earth's crust [1]. It is resistant to corrosion, exceptionally light and extraordinarily strong, weighing 60% of steel by volume [2]. Due to these properties, this metal is used to manufacture parts of airplanes, spaceships, missiles and ships [3]. In addition, the biocompatible property stands out because the tissues of the human body tolerate its presence, which is why it is currently widely used in the manufacture of materials used in medicine, such as hip and knee prostheses, bone screws, antitrauma plaques, dental implants, heart valves and pacemakers. In addition, this metal is the main component of surgical instruments, such as scalpels, scissors and staples [4]. However, high production costs of metallic titanium have limited its use in some industries [5]. Nevertheless, it remains in the aerospace and biochemical industries, where the advantages of using titanium outweigh its cost [2].

Titanium, in its metallic form, cannot be easily found in nature. The main concentrated sources of titanium are the ilmenite minerals ($FeOTiO_2$) and, with less content, the mineral deposits of sands,

such as rutile, anatase, leucoxene and brookite all with the $TiO_2$ formua [3,5,6]. The importance of titaniferous sands depends on the type of occurrence, the ability to extract the elements and the exploitation of particular natural products of industrial interest (such as rutile, zircon and ilmenite) [3].

Most of the world's production of titanium (95%) is used to obtain white titanium dioxide as a pigment to disperse light [5]. This pigment is produced by two traditional processes: sulfate process (40% of total $TiO_2$ production) and chloride process (60% of total $TiO_2$ production) [5,7]. Chlorinated processes generally use the so-called Kroll method, which consists of reducing titanium tetrachloride with ground magnesium in an argon atmosphere to prevent oxidation. $TiCl_4$ is previously obtained by a chlorination process at 700–1200 °C, in which the formed chlorides are separated by distillation [8]. Another method used to obtain this element from ilmenite is the processing of the mineral with concentrated $H_2SO_4$ in a closed vessel at 170–200 °C, obtaining a precipitate of relatively pure dehydrated $TiO_2$ [4]. Begum et al. conducted a study in which they leached black sand in an acidic medium for the dissolution of titanium. In their tests, roasting processes were carried out for 6 h at a temperature of 1000 °C by adding 0.5 g of ground anhydrous $Na_2CO_3$, after which the roasted material was contacted with $H_2SO_4$, varying the temperature, acid concentration and solid–liquid ratio. Finally, they concluded that the optimal operating conditions to achieve a 60% extraction of the titanium present in the sand were 120 min at 80 °C with 5 mol/L of $H_2SO_4$ [3].

On the other hand, the use of hydrochloric acid as a leaching agent, aimed at the benefit of the dissolution of titaniferous concentrates, has been the subject of numerous works considering concentrates of compositions, structures and textures that have very different reactivities and therefore diverse behaviors. Among them, we can mention those carried out by Tedesco and Rumi, who found that leaching in HCl is selective for Fe and Ti [9]. In this same medium, Tavani et al. managed to concentrate on the Ti residue, dissolving practically all the Fe present in the sands [10]. Years later, Sarno and Avanza proposed an appropriate method to leach titaniferous sands, which consists of successive leaching at low concentrations of HCl, thereby increasing the dissolution of Fe and decreasing that of Ti, achieving greater selectivity in the process [11]. These same authors also conducted kinetic studies in which they recommend that experiments must be carried out for each particular case, with the results only being appropriate to use for the design within the range of variables studied, due to the complexity of the sample [12].

In the present work, the reaction of titanium extraction from titaniferous sands in an acidic medium was comparatively studied. In addition, the effect of the operating parameters of the leaching reaction was investigated using a laboratory autoclave. In an effort to develop a novel route for titanium extraction from low-grade minerals, this will allow for a process that takes advantage of disused mining resources with low environmental impact.

## 2. Materials and Methods

### 2.1. Titanium Ore

The titaniferous sands used in this work were extracted from San Blas, located in the town of Bahía Blanca in the province of Buenos Aires, Argentina. The particle size used was −297 + 105 μm; the particle fraction was separated using sieves.

The characterization of the ore by X-ray diffraction (XRD) was carried out on a Rigaku D-Max III C diffractometer operated at 35 kV and 30 mA, using Cu $K\alpha$ radiation and Ni filter, $\lambda = 0.15418$ nm (Rigaku, Osaka, Japan). The experimental diffractograms were fitted with the software X'pert High Score 2.1.2, with $Al_2O_3$ (NYST) as reference.

Figure 1 shows the diffractogram of the titaniferous sands, in which it is observed that the mineralogical composition was as follows: ilmenite (ICDD 01-075-1212), magnetite (ICDD 01-088-0315), hematite (ICDD 01-089-2810), $Fe_2TiO_5$ (ICDD 01-087-1996), calcium silicate (ICDD 01-086-0401) and two quartz phases (ICDD 01-083-0541) and (00-033-1161).
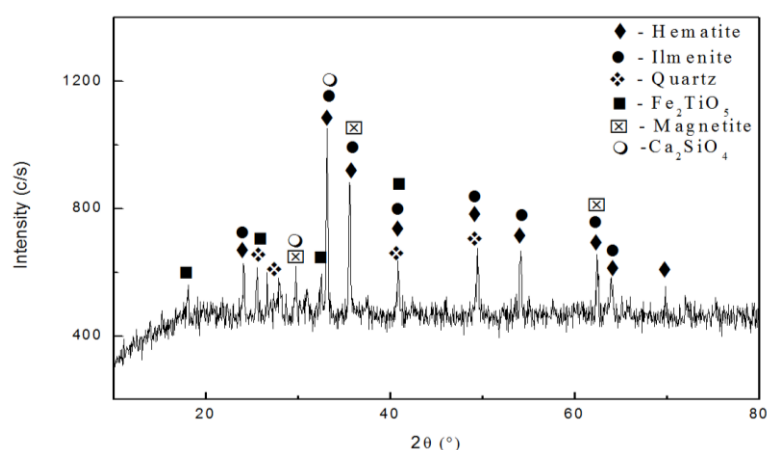
**Figure 1.** X-ray diffractogram for the titaniferous sand.

The titanium content of the sample of these titaniferous sands was 3.9%, as determined by X-ray fluorescence (XRF) in a Shimadzu EDX-8000 (Shimadzu, Kioto, Japan). This determination was performed by the method of standard addition. Using this calibration technique makes it possible to compensate and solve the effects of interference due to differences in the physical properties of the standard solutions and the sample and some interference by the matrix.

The ore morphology was studied through scanning electron microscopy (SEM) in a LEO 1450 VP microscope (Zeiss, Jena, Germany), and the semiquantitative composition of some particles was obtained by electron probe microanalysis (EPMA) using an EDAX energy dispersive X-ray spectrometer Genesis 2000 (EDAX, Mahwah, NJ, USA). Figure 2 shows a micrograph of the untreated mineral, previously calcined. It shows that the particles exhibit irregular edges and shapes, and some have flat faces. In Table 1, the EDS analysis of the particles marked in Figure 2 is shown.
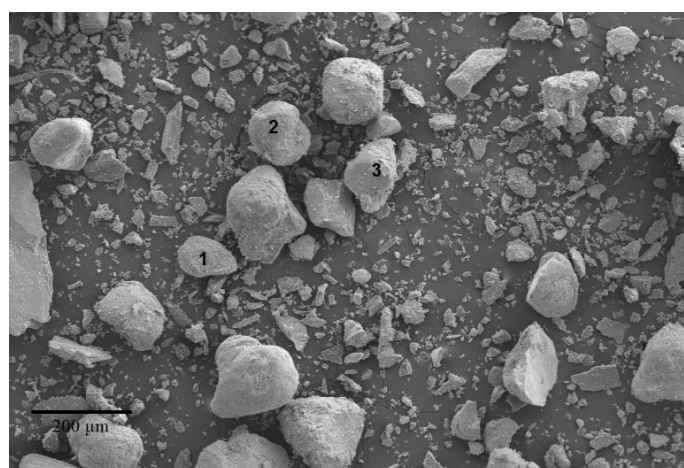


**Figure 2.** Micrograph of titaniferous sands prior to heat treatment.

**Table 1.** EDS analysis, in atomic percentage.

| Region Analyzed | %Fe | %O | %Ti | %Si | %Ca | %Mg | %Al |
|---|---|---|---|---|---|---|---|
| Point 1 | 61.4 | 29.7 | 3.9 | 2.6 | 0.5 | - | 1.9 |
| Point 2 | 49.74 | 20.78 | 1.79 | 20.62 | 2.91 | 4.16 | - |
| Point 3 | 44.04 | 18.1 | 2.03 | 26.25 | 3.46 | 5.09 | 1.03 |

The results of Table 1 state that these arenas have high Fe and O contents and small amounts of Si, Ti and Ca. The high Fe content is due to the presence of hematite and ilmenite, while the presence of Si

is due to the occurrence of the quartz and $CaSiO_4$ (calcium silicate) phases. Ti is present in the form of ilmenite and iron titanium oxide (pseudo brookite). Finally, Mg could come from the structure $MgSiO_3$ (enstatite). In addition, enstatite was not identified by XDR. These results are coincident with those obtained by XRD.

*2.2. Reactant and Leaching Tests*

The experimental tests were carried out in a Parr reactor, built in Monel alloy, with a capacity of 450 mL and equipped with electromagnetic agitation, a heating mantle and a control unit. To this device, 5 g of the sample and a volume of 275 mL of leaching solution were added. Then, $N_2$ (gas) was bubbled in order to remove air and thus reduce the corrosive effects on the reactor of $O_2$ dissolved in the hot HF medium.

The mixture was subsequently heated with stirring and a heating program between 5 and 10 °C/min, depending on the working temperature. The reaction time was measured from the moment the set temperature for each test was reached.

After the leaching tests, the reactor was allowed to cool for approximately 25 min without stirring. The reactor contents were subsequently filtered through blue band filter paper. Then, the paper with the unreacted solid was dried and calcined, and the resulting residue was stored for subsequent characterization by XRD, SEM and EDS.

Titanium was analyzed by XRF, using the calibration curve method to calculate the extraction percentage in all the experiments by the following equation:

$$\%X = \frac{Ti_f}{Ti_m} \, 100$$

where $Ti_m$ is the initial amount of Ti in the ore, and $Ti_f$ is the quantity of Ti from leach liquors.

The operating parameters studied were as follows: different acids (HF, $H_2C_2O_4$ and $H_2SO_4$) and mixtures of these acids (HF–$H_2C_2O_4$ and HF–$H_2SO_4$); leaching agent concentration, 5–20% *v/v*; temperature, 75–150 °C; time, 30–180 min; solid–liquid ratio, 0.9–3.6% *w/v*; stirring speed, 110–550 rpm.

The experimental study of this work was performed by univariate analysis. In order to evaluate the experimental error, each test was replicated three times. The average extraction efficiency and standard deviation were calculated for each parameter studied.

**3. Results**

*3.1. Type of Leaching Agent*

The leaching agents studied were HF, $H_2C_2O_4$, $H_2SO_4$, HF–$H_2C_2O_4$ and HF–$H_2SO_4$. In all tests, the other operating parameters were kept constant at the following values: temperature, 123 °C; reaction time, 80 min; solid–liquid ratio, 1.82% *w/v*; stirring speed, 330 rpm; concentration of the leaching agent(s) between 10% and 15% *v/v*. The obtained results are shown in Figure 3.

As seen in Figure 3, the best titanium extraction was achieved using the mixture of sulfuric acid–hydrofluoric acid and hydrofluoric acid at 123 °C. These results can be explained taking into account the high affinity of the $Ti^{4+}$ cation with the $F^-$ anion to form stable aqueous complexes to satisfy its coordination sphere, forming $[TiF_6]^{-2}$ complex, which in an acid medium forms $H_2[TiF_6]$ (Reactions 1 and 2) [8]. In the case of the HF/$H_2SO_4$ mixture, the effect is greater due to a synergistic effect, where firstly the HF acts according to Reactions 1 and 2, and then the $[TiF_6]^{-2}$ complex reacts with $H_2SO_4$ to give $Ti(SO_4)_2$ and HF (aq) which can react again with the titanium minerals in the titaniferous sands (Reaction 3). According to these results, these leaching agents were chosen to carry out the study of the other operative variables. From these results, the dissolution reactions of the

titanium ore with HF and $H_2SO_4$ were proposed, which would be the leaching agents that extract the titanium from both minerals:
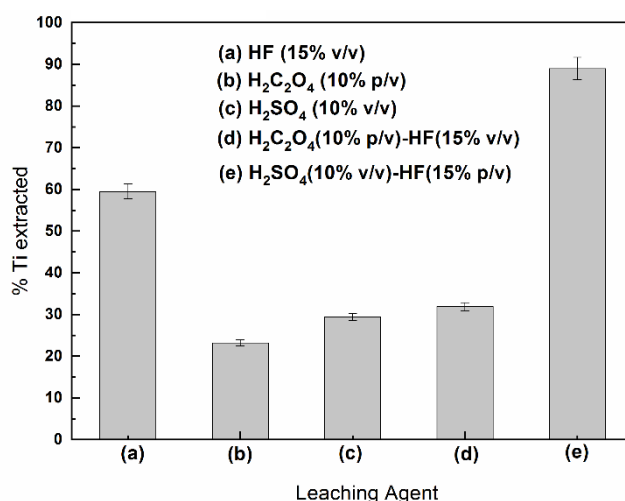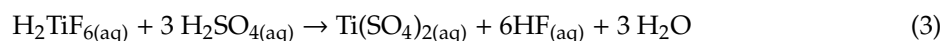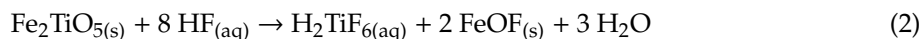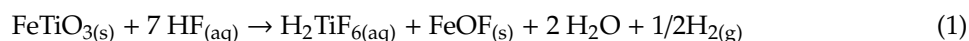
$$FeTiO_{3(s)} + 7\,HF_{(aq)} \rightarrow H_2TiF_{6(aq)} + FeOF_{(s)} + 2\,H_2O + 1/2H_{2(g)} \tag{1}$$

$$Fe_2TiO_{5(s)} + 8\,HF_{(aq)} \rightarrow H_2TiF_{6(aq)} + 2\,FeOF_{(s)} + 3\,H_2O \tag{2}$$

$$H_2TiF_{6(aq)} + 3\,H_2SO_{4(aq)} \rightarrow Ti(SO_4)_{2(aq)} + 6HF_{(aq)} + 3\,H_2O \tag{3}$$



**Figure 3.** Effect of the leaching agent.

These reactions were obtained using HSC Chemistry 5.1 software (Outotec,Espoo, Finland), based on the construction of the potential versus pH diagrams.

### 3.2. Temperature Effect

The results of the influence of temperature on the extraction reaction of titanium from the titaniferous sands are shown in Figure 4, working in the following conditions: solid–liquid ratio, 1.82% *w/v*; stirring speed, 330 rpm; reaction time, 80 min; leaching agents HF (15% *v/v*) and $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*).
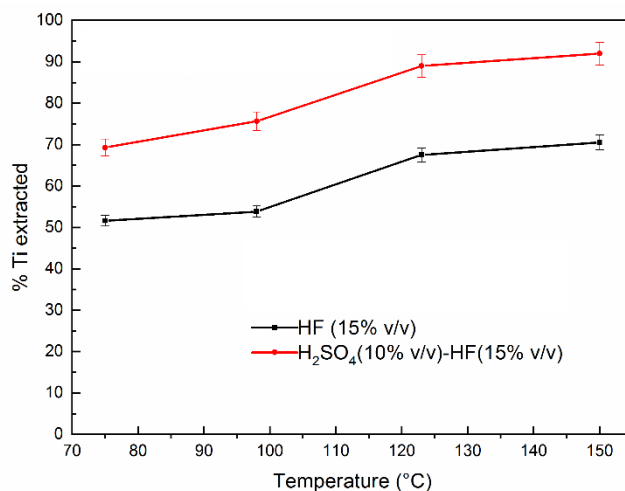


**Figure 4.** Effect of reaction temperature.

As seen in Figure 4, the increase in temperature leads to an increase in the dissolution of titanium. The highest extraction values are achieved by leaching with the mixture of sulfuric acid and hydrofluoric acid at 150 °C (92.0% and 70.5% respectively). However, important dissolution values are obtained at 123 °C for both leaching media. These results are as expected for a solid–liquid solution reaction since the magnitude of the dissolution of the metals present in the solid depends on the temperature (the general rule is that the increase of the temperature also increases the extent of the dissolution). In addition, it should be taken into account that the increase in temperature also increases the reactivity of solids [13–16]. Thus, 123 °C was selected to continue the study of the other operating parameters.

*3.3. Reaction Time Effect*

The results of the effect of time on the dissolution reaction of titanium are shown in Figure 5. The other operating parameters were kept constant at the following values: solid–liquid ratio, 1.82% *w/v*; stirring speed, 330 rpm; temperature, 123 °C; leaching agents HF (15% *v/v*) and $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*).
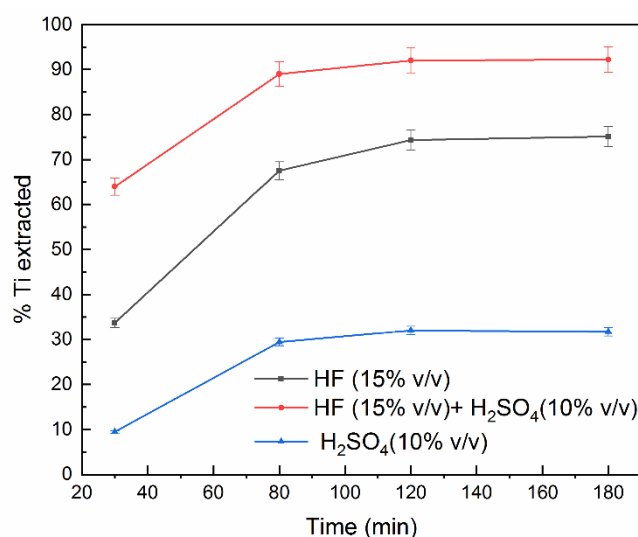


**Figure 5.** Effect of leaching time.

The results shown in Figure 5 show that the dissolution of titanium increases with the increase in reaction time, for the three leaching media studied. In addition, above 120 min of reaction, the plateau of the curve is reached. The synergistic effect can also be observed using the $HF/H_2SO_4$ mixture, since the extraction values are considerably improved if they are compared with the experiments that work with pure acids. The optimal extraction of titanium, 89%, was achieved at 80 min for the lixiviant $H_2SO_4$–HF medium (10% *v/v* and 15% *v/v*, respectively). These results are expected since fluid–solid reactive reactions are generally slow [13–16]. Similar results to ours were obtained by Das et al., Agatzini et al., Begum et al., Habashi, Nguyen and Lee and Haverkamp et al. [1–6], who conducted operating parameter studies on sands, mud and minerals with sulfuric and hydrochloric media, finding in all cases that the increase in reaction time increases the dissolution of these materials.

*3.4. Concentration Effect of Leaching Agents*

The ore leaching tests with different concentrations of acids and mixtures were performed under the following conditions: solid–liquid ratio, 1.82% *w/v*; stirring speed, 330 rpm; reaction time, 80 min; temperatures, 75 and 123 °C. The results obtained are shown in Figure 6.
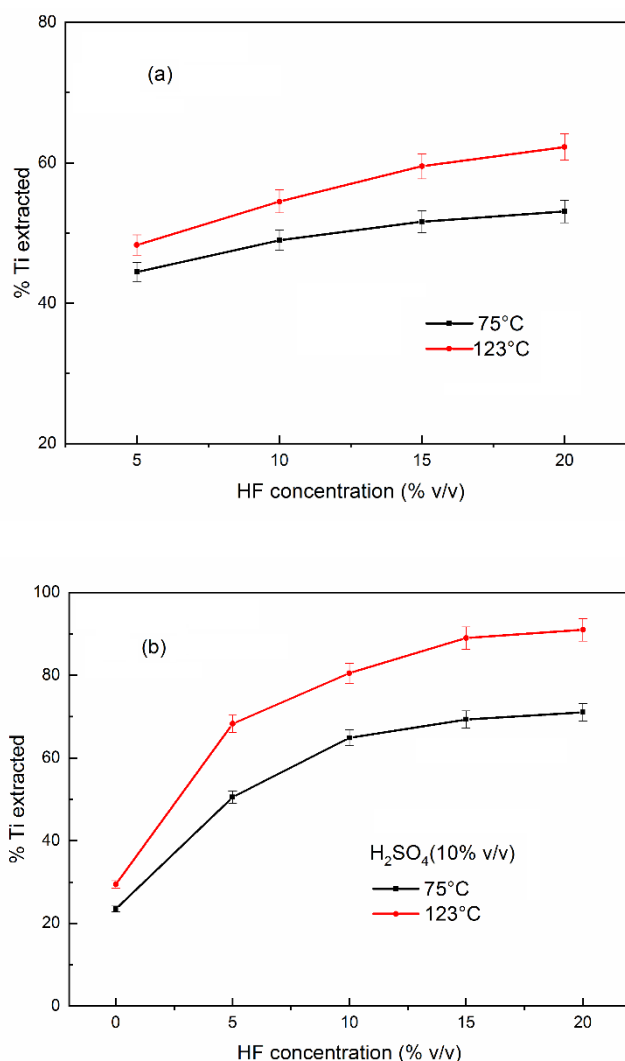
**Figure 6.** Effect of the concentration of the leaching medium at 75 and 123 °C: (**a**) HF; (**b**) $H_2SO_4$ (10% *v/v*)–HF.

Figure 6 shows that the dissolution of titanium increases with the increase in the concentration of leaching agent. This is because the extent of solid–fluid reactions, in which soluble products are formed, depends on the concentration(s) of the leaching agent(s). In addition, this phenomenon is favored by the increase in temperature, which not only increases the activity of the ions responsible for the dissolution of the solid but also increases the solubility of the compounds formed. These results are similar to those found by Das et al., Agatzini et al., Begum et al., Habashi, Nguyen and Lee and Haverkamp et al. [1–6]. They reported that the increase in the concentration of acid leads to high extraction percentages of Ti in the leaching tests of minerals, red mud or black sands with HCl or $H_2SO_4$. On the other hand, comparing Figure 6a,b, it is observed that when using the mixture of HF and $H_2SO_4$, better titanium extraction values are obtained for both temperatures (89% and 71% for 123 and 75 °C, respectively) with $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*) than with HF (15% *v/v*) (Figure 6b).

*3.5. Solid–Liquid Ratio Effect*

Figure 7 shows the effect of the solid–liquid ratio on the extraction of titanium. In all the tests, the other operating parameters were kept constant at the following values: temperature, 75 and 123 °C; reaction time, 80 min; stirring speed, 330 rpm; $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*) or HF (15% *v/v*) leaching agents.
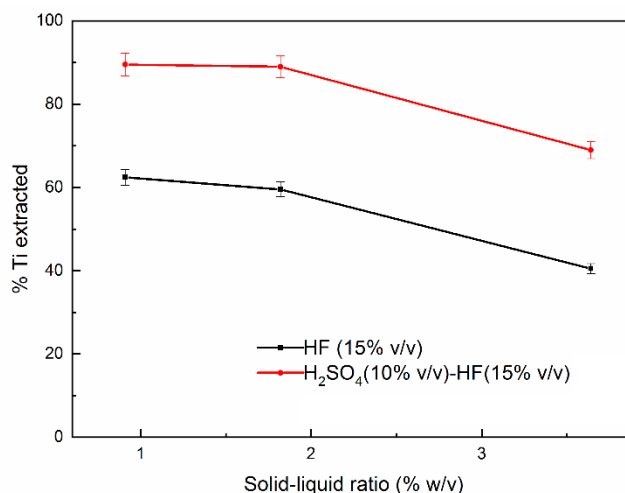
**Figure 7.** Effect of solid–liquid ratio.

The results of Figure 7 show that increasing the solid–liquid ratio decreases the dissolution of titanium, which is due to the leachate becoming saturated as the content of dissolved metals increases owing to the increase in the solid–liquid ratio, for a fixed volume of liquid. This hinders the interaction between the leaching agent and the sample, thus decreasing the leaching reaction.

### 3.6. Stirring Speed Effect

Figure 8 shows the effect of the stirring speed on the extraction of titanium. The other parameters were kept constant at the following values: temperatures, 75 and 123 °C; reaction time, 80 min; solid–liquid ratio, 1.82%; $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*) or HF (15% *v/v*) leaching agents.
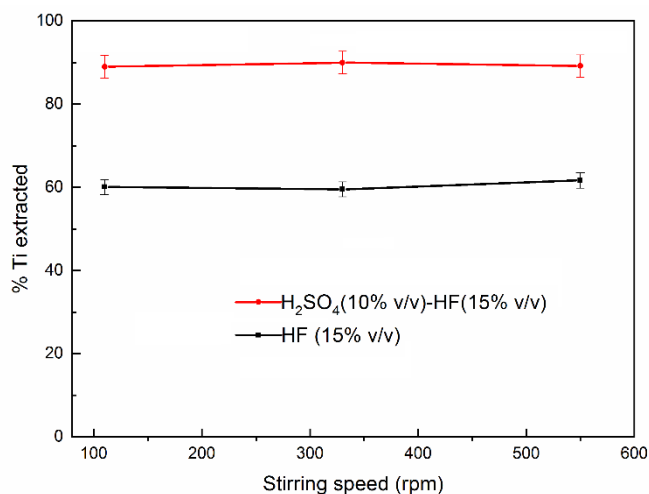


**Figure 8.** Effect of stirring speed.

The results of Figure 8 indicate that the increase in the stirring speed slightly affects the titanium dissolution, which would allow us to say that the transfer of mass (or leaching agent) through the boundary layer (Nernst layer) is maximal [13–16].

### 3.7. Residues Characterization

The characterization of the residues was performed by XRD, SEM and EDS. Figure 9 shows the XRD of the waste from different leaching conditions.
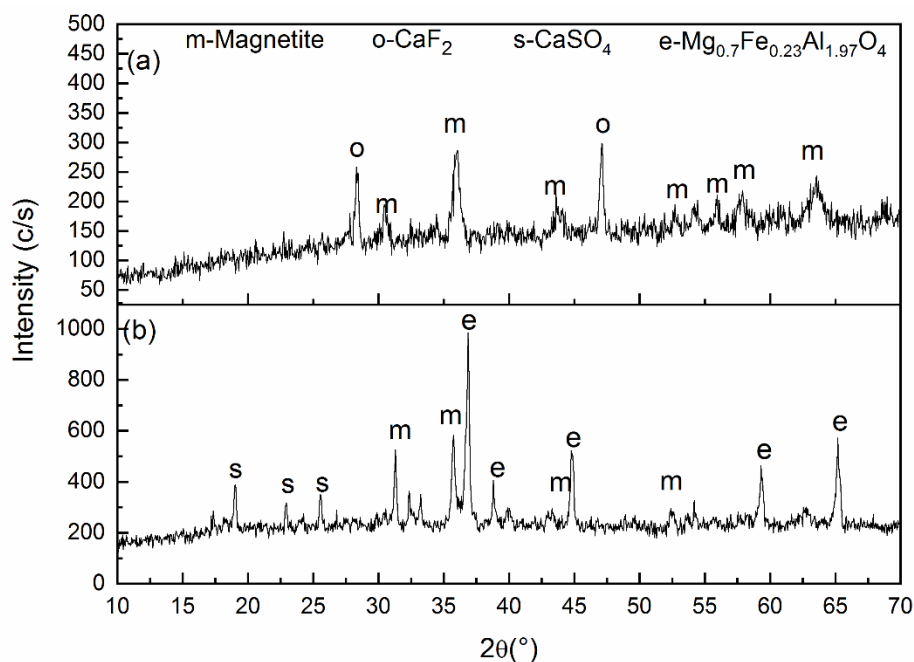
**Figure 9.** XRD of the residues at 123 °C: (**a**) HF; (**b**) HF (15% *v/v*)-$H_2SO_4$ (10% *v/v*).

In the diffractograms of Figure 9, there are no diffraction lines that fit the structures of some of the titanium compounds, which is consistent with the high titanium extraction values achieved in the leaching test. In the diffractogram of the residue from dissolution in HF medium (Figure 9a), the presence of fluorite and magnetite was observed. In the XRD obtained after treating the mineral with HF–$H_2SO_4$ (Figure 9b), diffraction lines corresponding to magnetite, a mixed oxide of Fe, Al and Mg, and calcium sulfate were detected.

The presence of the calcium compounds in the diffractograms of the residues can be explained, taking into account that, in addition to the dissolution of ilmenite and the titanium oxide and iron, leaching of the accessory minerals occurs, including the metal contained. This leads, according to the leaching media, to the formation of $CaSO_4$ and $CaF_2$. In addition, the formation of mixed oxide is due to the reaction of iron oxyfluoride (Reaction 2) with magnesium and aluminum from the dissolution of anorthite and enstatite ($MgSiO_3$).

Figures 10 and 11 show the SEM micrographs of two residues obtained under different leaching conditions.
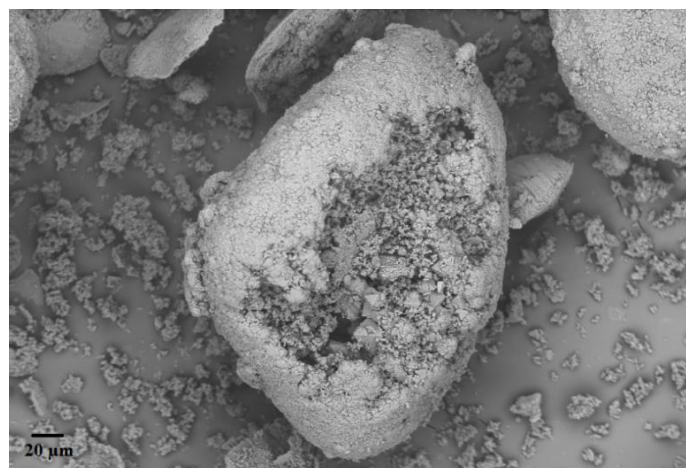


**Figure 10.** Micrograph of the leaching residue at 123 °C with 15% *v/v* HF.
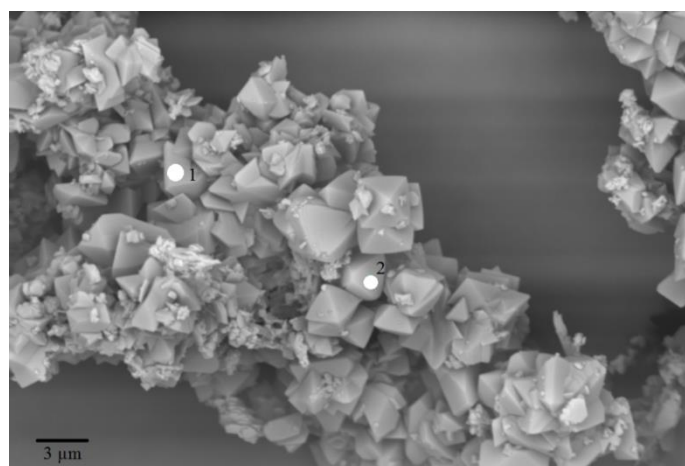
**Figure 11.** SEM of the leaching residue at 123 °C, with HF (15% *v/v*)–$H_2SO_4$ (10% *v/v*).

Figure 10 shows the micrograph of the residue, where it can be seen that the ore particles are selectively attacked over an area; around the particle, small fragments of the disintegrated mineral are seen due to the progress of the reaction.

Figure 11 shows the micrograph of the leaching residue at 123 °C, with $H_2SO_4$ (10% *v/v*)–HF (15% *v/v*), where the formation of a rhombic crystalline structure can be seen. An EDS analysis was performed on different points of this particle. The results are presented in Table 2.

**Table 2.** EDS analysis, in atomic percentage.

| Sector Analyzed | %Fe | %O | %Mg | %Al | %Ca |
|---|---|---|---|---|---|
| Point 1 | 61.4 | 29.7 | 8.3 | 0.30 | 0.5 |
| Point 2 | 55.3 | 30.5 | 7.5 | 0.28 | 0.3 |

The EDS analysis of the particles corresponding to this phase (marked particles) indicates that they have a high content of oxygen, aluminum, iron and magnesium, while in smaller quantity we also find the presence of aluminum and calcium. These results indicate that these particles would correspond to the structure of the mixed oxide $Fe_{0.7}Al_{0.23}Mg_{1.97}O_4$ that has been identified by XRD. The formation of iron compounds during leaching can benefit the subsequent recovery of titanium in a next stage of the process.

## 4. Conclusions

In this study, the results of the extraction reaction of titanium from titaniferous sands with different leaching agents are presented. The main findings of this study are the following: the leaching media composed of HF or a mixture of $H_2SO_4$–HF produces important extractions of titanium in the working conditions investigated. The leaching temperature, time, concentration of the fluid phase and the solid–liquid ratio have a marked influence on the extraction reaction of titanium contained in these titaniferous sands. The stirring speed, between 110 and 550 rpm, has a slight effect on the solid extraction reaction. The optimal conditions to achieve of 89% extraction of titanium were obtained to be as follows: HF (15% *v/v*)–$H_2SO_4$ (10% *v/v*) as leaching agent; temperature of 123 °C; reaction time of 80 min; solid–liquid ratio of 1.82% *w/v*; stirring speed of 330 rpm. The analysis of the leaching residues corroborated that no titanium precipitate is formed during the dissolution of the ore. In addition, precipitation of iron compounds occurs, which can then favor the recovery process of titanium from leach liquor in a next stage of the process.

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G.D.R., N.T., F.M.T. and M.H.R.; investigation, G.D.R., F.M.T. and M.H.R.; resources, M.H.R.; data curation, E.G.P. and G.D.R.; writing—original draft preparation, M.H.R. and G.D.R.; writing—review and editing, E.G.P., N.T., F.M.T., G.D.R. and M.H.R.; visualization, G.D.R. and M.H.R.; supervision, M.H.R.; project administration, M.H.R.; funding acquisition, N.T. and M.H.R. All authors have read and agreed to the published version of the manuscript".

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