

Review

Recent Progress in Electric Furnace Titanium Slag Processing and Utilization: A Review

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Abstract: Titanium slags produced through ilmenite electric furnace smelting contain 60–80% TiO₂, a vital titanium resource in the titanium industry. The processing and utilization of titanium slag is faced with many challenges, such as complex mineral structures, high requirements, severe environmental pollution, and heavy additives and energy consumption. This study aims to review the technologies for the processing and utilization of titanium slag. First, we analyze the characteristics of titanium slag from different regions. Then, we discuss in detail the methods for processing and using titanium slag. The progress in electric furnace titanium slag processing and utilization can be divided into two areas: the preparation of titanium dioxide and high-quality titanium-rich materials. These include H₂SO₄ leaching, HCl leaching, fluoride leaching, sulfur roasting–leaching, alkaline roasting–leaching, oxide roasting–leaching, oxidation and reduction roasting–leaching, phosphorylation roasting–leaching, and ammonia decomposition leaching. Further development of oxide roasting–leaching for the extraction of titanium from titanium slag is recommended.

Keywords: titanium slag; electric furnace smelting; extraction titanium; leaching



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1. Introduction

Titanium is the ninth most abundant chemical element on earth and it plays a vital role in manufacturing paint, plastics, pigments, paper, cosmetics, airplanes, and space ships [1–4]. Ilmenite is the primary titanium resource, accounting for ~89% of titanium mineral consumption worldwide in 2020. According to the USGS statistics of 2020, ilmenite resources exceeded 7.8 billion tons worldwide. Figure 1 illustrates the distribution of ilmenite resources in the world; these distributions are to be found in [5]. The USGS statistical results also predicted that the annual production of ilmenite would be close to 3800 kilotons in 2020, and that by 2020, the annual accumulation limit of titanium slag would be close to 3100 kilotons (as shown in Figure 2). More than 65% of ilmenite is smelted using electric furnaces worldwide and 85% in China, where it is the primary production method for ilmenite [6]. Ilmenite is smelted in an electric furnace to obtain electric furnace titanium slag (containing 60–80% TiO₂) and semi-steel [7]. Therefore, the means by which to upgrade titanium slag for processing and utilization is an issue of concern.

Many studies have researched the extraction of titanium from titanium slag. The progress of electric furnace titanium slag processing and utilization can be divided into two areas. Titanium dioxide is prepared through sulfuric acid leaching, hydrochloric acid leaching, fluoride leaching, and ammonia decomposition. High-quality titanium-rich materials are prepared through sulfide roasting–leaching, alkaline roasting–leaching, oxidation roasting–leaching, redox roasting–leaching, and phosphoric acid roasting–leaching. Much research has been conducted on the processing and utilization of titanium slag. However, there have been few systematic summaries and comparative analyses on the current methods of the comprehensive utilization of titanium slag from electric furnaces. A critical review of the methods for extracting titanium from titanium slag was proposed in the

present study. There are three primary purposes of the current work: (1) to analyze the ilmenite resources, titanium slag production, and its chemical/physical characteristics; (2) to review the relevant methods for extracting titanium; and (3) to summarize the technical challenges of extracting titanium and provide valuable guidelines for extracting titanium from titanium slag.

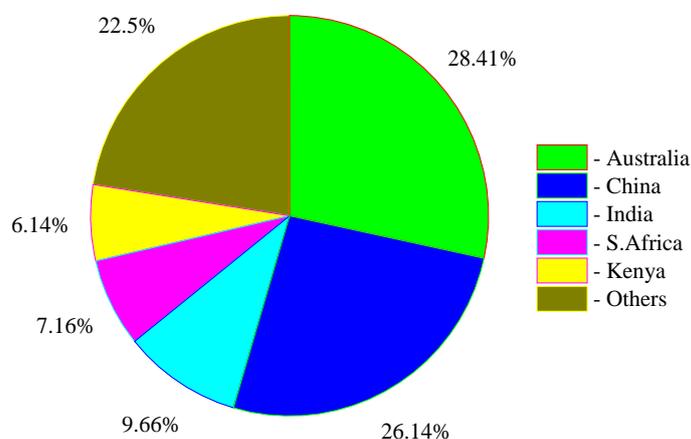


Figure 1. Global distribution of ilmenite reserves.

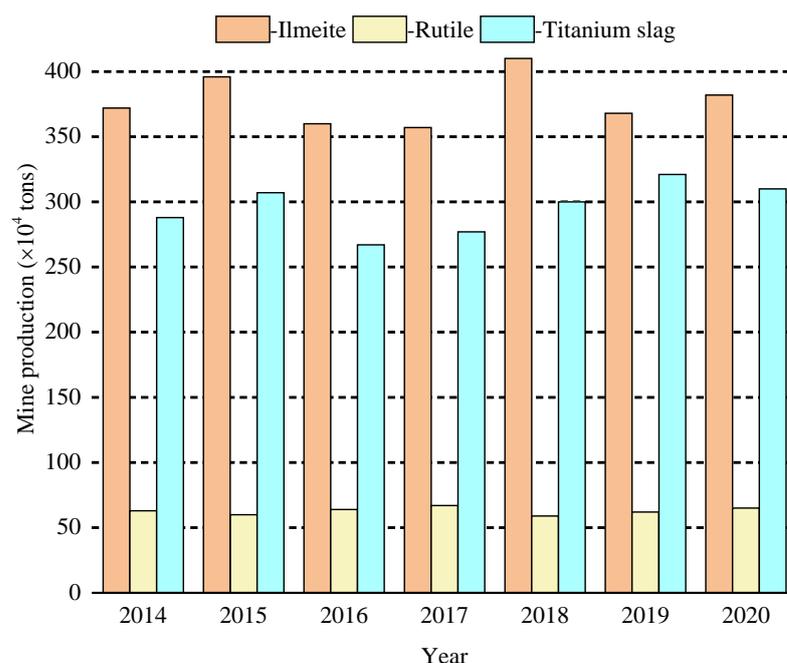


Figure 2. The annual production of the ilmenite and titanium slag around the world.

2. Titanium Slag Production and Characteristics

Titanium slag is obtained through ilmenite electric furnace smelting; its typical process flow diagram is shown in Figure 3. Generally, there are a multitude of phases in titanium slag, such as $M_xTi_{3-x}O_5$ ($0 < x < 2$, $M = Ti, Fe, Al, Mg$, etc.), rutile, augite, and metallic iron, and the impurities in titanium slag are difficult to remove through leaching [8,9]. In particular, the titanium slag in Panzhihua cannot be used because of its high calcium and magnesium contents [10,11]. As shown in Table 1, a comparison of the chemical compositions of titanium slag from different regions is presented. The contents of TiO_2 exceed 70%, and calcium, magnesium, and silicon are the main impurities. A quantitative analysis of the physical phase in the titanium slag of the electric furnace was carried out. Table 2 shows the phases present in titanium slag. The content of anovosite was 86.6%, that of olivine and enstatite was 5.8%, and that of the silicate glass was 2.5%.

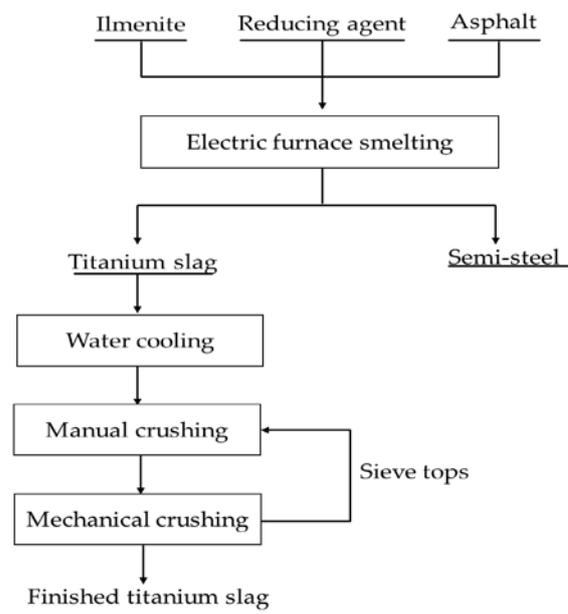


Figure 3. Typical process flow diagram of ilmenite smelting with an electric furnace.

Table 1. Comparison of the chemical composition of titanium slag in different regions.

	TiO ₂	Fe	CaO	MgO	Al ₂ O ₃	SiO ₂	Ref
Rio Tinto	78.5	7.73	0.66	5.57	2.36	2.75	[4,12]
QIT	80	9	0.6	5	2.9	2.4	[13,14]
Tinfos	75.4	7.6	0.66	7.92	1.19	5.35	[15]
RBM	85.5	9.4	0.14	0.9	2.0	1.5	[15]
Indian rare-earth Limite	79.21	16.75		0.34	1.43	1.1	[16]
Panzhuhua	72.43	9.26	0.86	3.12	2.55	7.39	[17]
YunNan	86.37	2.36	<0.05	1.32	6.16	4.66	[18]

Table 2. Phase present in the Panzhuhua titanium slag.

Minerals	Anosovite	Ilmenite	Anatase	Metallic Iron	Olivine and Enstatite	Glass	Others
Content/%	86.6	2.5	0.2	1.4	5.8	2.4	0.2

According to V. Grass et al., the primary anosovite phase found in titanium slag from electric furnace smelting has a pseudobrookite-type structure with lattice parameters $a = 9.8111 \text{ \AA}$, $b = 3.7509 \text{ \AA}$, $c = 9.9468 \text{ \AA}$, and $\beta = 90.628 \text{ \AA}$ [19]. The high-temperature monoclinic Ti₃O₅ structure matching the space group C2/m showed an excellent agreement with the results when the powder X-ray diffractometry (PXRD) was examined. The anosovite belongs to the orthorhombic system and its space groups D_{2h}¹⁷-Cmcm (63), Z = 4. In the system, the TiO₆ octahedron is linked with Ti⁴⁺ and the TiO₆ octahedron co-located with it to generate (TiO₅) single strands are linked to each other by a M³⁺ extending along the C-axis. The octahedral voids between TiO₅ chains can be deformed over a wide range, leading to many in-phase permutations and solid solutions [20]. Anosovite is the key to extracting titanium from titanium slag.

3. The progress of Titanium Slag Processing and Utilization

3.1. Preparation of Titanium Dioxide

There are many methods for preparing titanium dioxide from titanium slag, including sulfuric acid leaching, hydrochloric acid leaching, fluoride leaching, and ammonia decomposition. Table 3 compares these methods in terms of raw materials, reaction temperatures,

waste residues and liquids, degree of reagent recycling, and product crystallization. The method of preparing titanium dioxide from titanium slag is analyzed and summarized in detail in this sub-section.

Table 3. The comparison of preparation methods of titanium dioxide.

Methods	Raw Material	Reaction Temperature	Waste Liquid and Residue	Reagent Cycle	Product Crystals	Ref
H ₂ SO ₄ leaching	Titanium concentrate and titanium slag	120~250 °C	Acid hydrolysis residue, waste acid, acid waste water	Some sulfuric acid can be recycled	Anatase and rutile	[21,22]
HCl leaching	Ilmenite and titanium slag	80~100 °C	Acid hydrolysis residue, acid waste water	Hydrochloric acid can be recycled	Anatase and rutile	[23]
Fluoride leaching	Ilmenite, perovskite, rutile, high titanium slag, etc.	100~140 °C	Thermal hydrolysis residue	Fluorinated reagents can be recycled	Anatase and rutile	[24]
Ammonia decomposition leaching	High titanium slag	150 °C	Waste residue and ammonia	Ammonia can be recycled	Anatase	[25]

3.1.1. H₂SO₄ Leaching Process

In the sulfate process, titanium slag is digested with sulfuric acid to form water-soluble sulfates (titanyl sulfate TiOSO₄ and iron sulfates). The soluble sulfates are later hydrolyzed and precipitated to form titanium dioxide pigments. The flow diagram of the sulfate process is shown in Figure 4. During the H₂SO₄ leaching process, the main reactions are as follows:

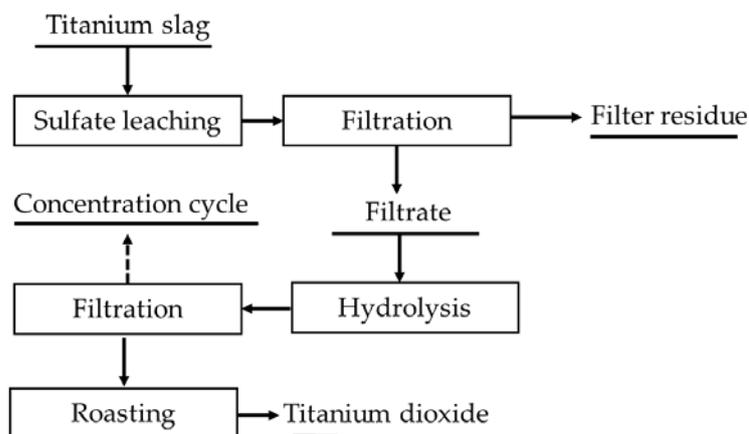
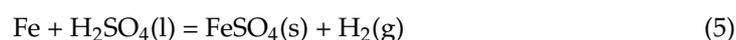
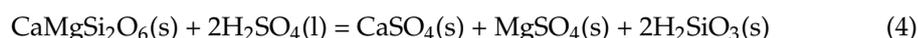
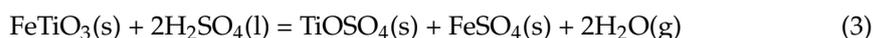


Figure 4. The flow diagram of sulfate process.

The sulfate process was the first commercialized technology to convert ilmenite to titanium pigment. From this point of view, upgrading the titanium slag through H₂SO₄ leaching was proposed [26,27] in 1994. Nie [28] examined the mechanism and kinetics of the sulfuric acid leaching of titanium from titanium-bearing electric furnace slag to better

understand the operating conditions for extracting titanium from titanium slag. Under the conditions of an average particle size of 31.5m, an acid/solid ratio of 2.0:1, an initial acid concentration of 88.0 wt.%, a reaction temperature of 513.15 K, and a water leaching temperature of 333.15 K for 120 min, the Ti leaching rate achieved was 89.46%.

Yan [29] investigated the behavior of a two-step sulfuric acid leaching process of a Ti-bearing blast furnace slag. The results indicated that the slag was pre-leached with a 20% sulfuric acid solution. Most of the aluminum was composed of approximately 64% magnesium and 46% titanium at this stage. After pre-leaching, the residue was further leached with the help of mechanical milling, resulting in a total Ti leaching rate of over 94%. Qu [30] also reported that more than 84.29% of the total obtained under the condition of sulfuric acid leaching had a particle size <0.045 mm, a 90 wt.% sulfuric acid concentration, an acid/slag mass ratio of 1.6:1, a feeding temperature of 120 °C, a reaction temperature of 220 °C, a reaction time of 120 min, and curing at 200 °C for 120 min.

The sulfuric acid process has a long process flow, low product quality, and significant waste emissions. Waste emissions, in particular, are the biggest challenge facing the development of titanium dioxide using the sulfuric acid process. Reducing the “three waste” emissions and by-products will provide reasonable and practical recycling and improving the environmental protection of the process is the focus of future development of the sulfuric acid process of titanium dioxide. In summary, titanium extraction from titanium slag through the sulfuric acid leaching process has poor recovery and high costs, which needs further improvement.

3.1.2. HCl Leaching Process

The hydrochloric acid titanium dioxide process uses hydrochloric acid to acidify titanium slag. The acid solution is purified and de-polluted to obtain titanium liquid, which is then hydrolyzed to obtain metatitanic acid, which is treated with salt, calcined, and post-treated to obtain titanium dioxide products. The flow chart of the hydrochloric acid leaching process is shown in Figure 5. In the process, the main reactions are as follows [31]:

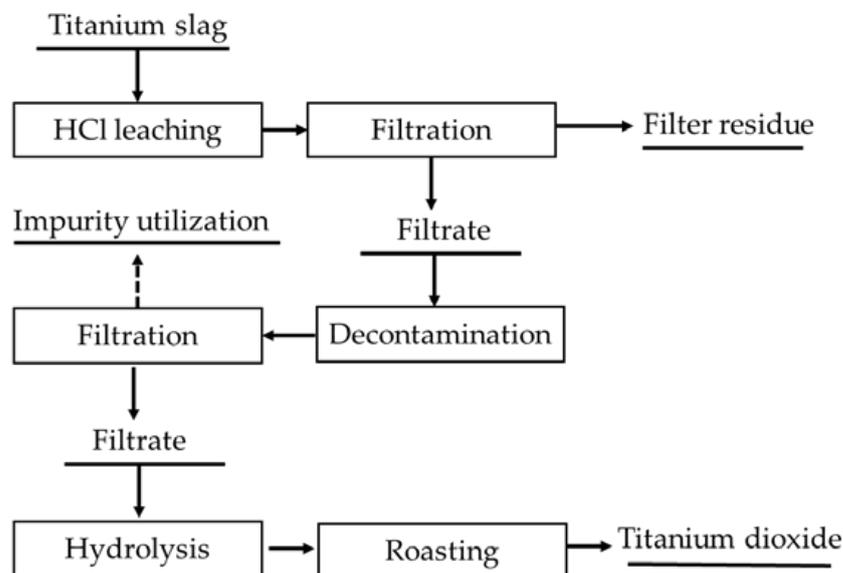
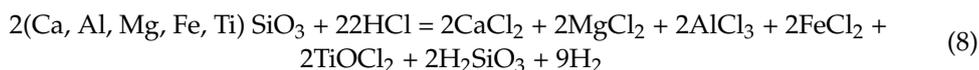
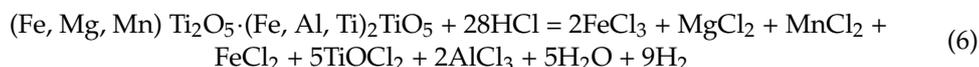


Figure 5. The flow diagram of hydrochloric acid leaching process.

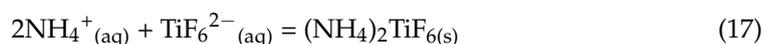
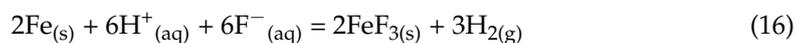
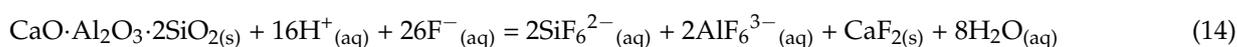
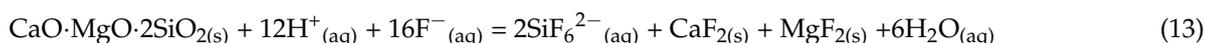
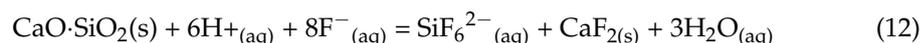
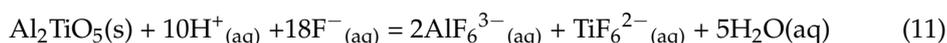
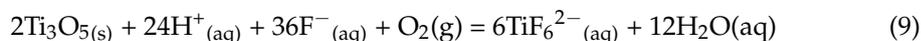
For HCl leaching, Samal previously described the preliminary procedures for leaching titania-rich slag in hydrochloric acid [32]. The findings suggest that reagents that inhibit titanium hydrolysis and polymerization promote the dissolution of titanium slag in solution. Samal [33] also investigated the effect of phenol and resorcinol on titanium slag hydrochloric acid leaching. Resorcinol combined with ethylene glycol performs better as a better additive in the leaching of titanium slag.

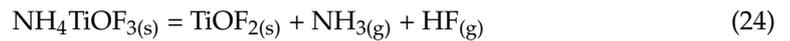
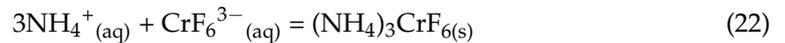
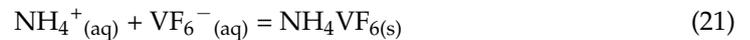
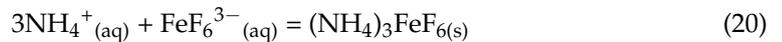
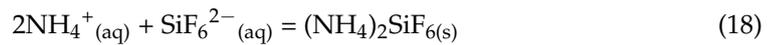
According to Xiong [34], the dissolution rate of various minerals in slag decreases in the order of spinel, diopside, and perovskite. Along with the quick breakdown of spinel and diopside, the slag breaks into a large number of tiny particles, the most common of which is perovskite. After 8 h in a 20% hydrochloric acid solution at 100 °C, the dissolved percentage of titanium is only 44%. Zhou also [35] investigated the maximum recovery yield of titanium, which was approximately 96%, and the content of titanium in the acid leaching residue exceeded 37% using a 150/75 µm particle size at an 80 °C reaction temperature and a 20:1 liquid–solid ratio for a 90 min reaction time with 5mol/L hydrochloric acid concentration. Zheng [36] investigated the kinetic behavior during hydrochloric acid leaching, and the findings revealed that the rate of dissolution was controlled by a chemical process.

The hydrochloric acid leaching process can effectively dissolve all elements in the titanium slag. Concentrated hydrochloric acid must be used in the acid digestion process, and the efficiency of the acid digestion system decreases significantly when the mass fraction of hydrochloric acid is below 30%. Secondly, the low evaporation temperature of concentrated hydrochloric acid and the low evaporation temperature of the acid causes corrosion to the equipment and increases the amount of hydrochloric acid used. The concentration of hydrochloric acid obtained from the subsequent hydrolysis of the leaching product is not 20%, making it difficult to achieve a closed circuit. The technology used to remove impurities by extraction is immature, the two-phase partitioning of the extractant is slow, and the extractant is expensive. The solution contains a series of impurities, leading to the final product being of low quality. In addition, the process requires a high concentration of hydrochloric acid, which brings with it severe equipment corrosion and a high cost.

3.1.3. Fluoride Leaching Process

The fluoride leaching process was deemed a promising method for titanium pigment production. The fluoride leaching process was first published by Gordienko [37]. The titanium ore was reacted with an aqueous NH_4F and NH_4HF_2 solution, filtering the solid residue and an aqueous solution by consequent separation. The aqueous solution was subjected to hydrolysis, the solid residue was subjected to pyrohydrolysis, and a high-quality titanium oxide was obtained. The reactions that may be involved in the fluoridation leaching process are as follows:





Bakeeva [38–40] investigated the system of $(\text{NH}_4)_2\text{TiF}_6$ - $(\text{NH}_4)_3\text{FeF}_6$ - NH_4F - H_2O , $(\text{NH}_4)_2\text{TiF}_6$ - $(\text{NH}_4)_3\text{FeF}_6$ - NH_4F - H_2O_2 , and $(\text{NH}_4)_2\text{TiF}_6$ - $(\text{NH}_4)_2\text{SiF}_6$ - NH_4F - H_2O solution behavior. The results showed that by coprecipitating $(\text{NH}_4)_3\text{TiO}_2\text{F}_5$ and $(\text{NH}_4)_3\text{FeF}_6$ as a result of the crystallochemical substitution of Fe^{3+} for Ti^{4+} , the amount of Fe (III) salts in the system of $(\text{NH}_4)_2\text{TiF}_6$ - $(\text{NH}_4)_3\text{FeF}_6$ - NH_4F - H_2O could be reduced. The $(\text{NH}_4)_2\text{SiF}_6$ in the system of $(\text{NH}_4)_2\text{TiF}_6$ - $(\text{NH}_4)_2\text{SiF}_6$ - NH_4F - H_2O was discovered in bararite form, not the cryptohalite form corresponding to the alteration of the initial silicon salt. The isovalent isomorphous substitution of Si^{4+} ions for Ti^{4+} in the combination TiF_6^{2-} causes this transfer.

According to Zheng [41], 98.84% titanium in TEFS was extracted at an optimum leaching temperature of 140 °C, a concentration of 12 mol/L, a liquid/solid mass ratio of 10, and a leaching time of 60 min. Titanium, iron, and silicon were dissolved in the fluoride solution as TiF_6^{2-} , FeF_6^{3-} , and SiF_6^{2-} , respectively, during the process. Fluoride reacted with aluminum, magnesium, and calcium to form the precipitates of $(\text{NH}_4)_3\text{AlF}_6$, $\text{CaMg}_2\text{Al}_2\text{F}_{12}$, $\text{NH}_4\text{MgAlF}_6$, and CaF_2 . The process is described in Figure 6.

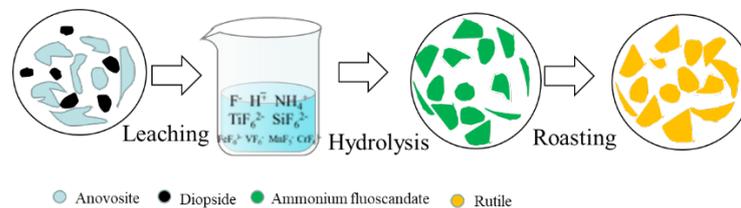
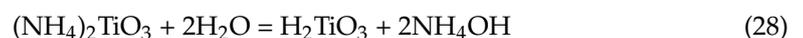
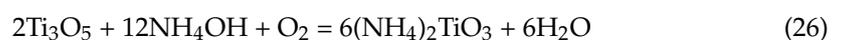


Figure 6. The schematic diagram of the reaction mechanism in titanium slag using fluoride leaching.

Compared with other leaching processes, the fluoride leaching process has desirable prospects because all kinds of feedstocks can be handled, and the product of TiO_2 meets a high grade. Unfortunately, there are few research reports on recycling fluoride solutions.

3.1.4. Ammonia Decomposition–Leaching Process

For titanium dioxide preparation through ammonia decomposition, titanium slag is mixed with a specific proportion of ammonia to a particular temperature. Titanium slag is then destroyed by ammonia decay to produce water-soluble titanate ammonia, water is immersed into the solution, then thermal hydrolysis of the precipitation occurs to form titanate acid after the subsequent titanium dioxide is obtained through calcination. The flow chart of ammonia decomposition to prepare titanium dioxide is shown in Figure 7. The reactions that may be involved in the fluoridation leaching process are as follows.



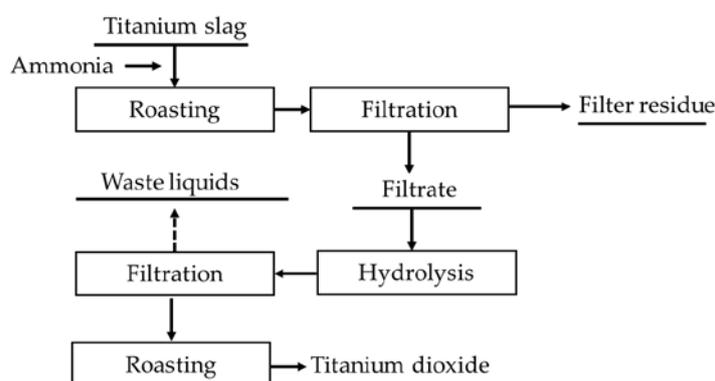


Figure 7. The flow diagram of the preparation titanium dioxide using ammonia decomposition.

The ammonium hydroxide decomposition process of titanium slag was proposed by A.A. Nayl [25] in 2009. The process begins with the hydrothermal decomposition of titanium slag with NH_4OH to form ammonium titanate $(\text{NH}_4)_2\text{TiO}_3$, which is then acidified with distilled water and hydrolyzed to produce high-purity titanium oxide. Approximately 99.8% high-purity anatase TiO_2 was obtained with 4 M NH_4OH at a temperature of 150 °C. A. A. Nayl [25] also reported the kinetics of the decomposition reaction, which revealed that the reaction was chemically controlled with an apparent activation energy of 27.8 ± 1.6 kJ/mol.

Fewer studies have investigated the mechanism of upgrading titanium slag through ammonia hydroxide decomposition. The decomposition of titanium slag in ammonia roasting must take place in a closed environment. Ammonia decomposes quickly. To ensure that the reaction is carried out thoroughly, ammonia must be constantly added. The problems of poor process stability in the manufacturing process, more severe ammonia corrosion of the equipment, and environmental pollution are exceptionally difficult to address, and the method implementation is complex.

3.2. Preparation of High-Quality Titanium-Rich Materials

There are many methods for preparing titanium-rich materials from titanium slag, including sulfated roasting–leaching, alkaline roasting–leaching, oxidized roasting–leaching, redox roasting–leaching, and phosphoric acid roasting–leaching. Table 4 shows a comparison of the advantages and disadvantages of different methods of preparing titanium-rich materials. The feasibility analysis of each method and the current status is summarized in depth in the respective sub-sections.

Table 4. Comparison of the different methods of preparing titanium-rich materials.

Methods	Reaction Temperature	TiO_2	Additives	(CaO, MgO) Removal Rate/Content	Waste Residues, Waste Liquids, and Waste Gases	Ref.
Sulfur roasting–leaching	300~800 °C	>98%	$\text{SO}_2/(\text{NH}_4)_2\text{SO}_4$	91.9%, 91.4%	Acid water, sulfate NH_3/SO_2 ,	[42]
Alkaline roasting–leaching	800~1000 °C	>99%	$\text{NaOH}/\text{NaHCO}_3/\text{Na}_2\text{CO}_3$	91.5%, 89.7%	Alkaline waste water, alkali salts	[43,44]
Oxide roasting–leaching	1200~1550 °C	98%		96.5%, 94.3%	Acid water	[45]
Oxide and reduction roasting–leaching	800~1000 °C	>99%		93.1%, 94.5%	Acid water	[46]
Phosphorylation roasting–leaching	800~1200 °C	94%	H_3PO_4	87.19%, 94.68%	Acid water, phosphate	[47]

3.2.1. Sulfur Roasting–Leaching Process

The sulfur roasting–leaching process was first developed by Elger [48–51]. The admixture sample reacts with SO_3 or mixed SO_2 – O_2 gases at an elevated temperature to form sulfates of the impurities and then it leaches the sulfates from the reaction product with water, with the oxide impurities in the titanium slag being removed. The leached titanium oxide sulfate is hydrolytically transformed through high-temperature calcination to produce rutile. The process can be described in Figure 8. The chemical reactions that may occur during the roasting process are shown below:

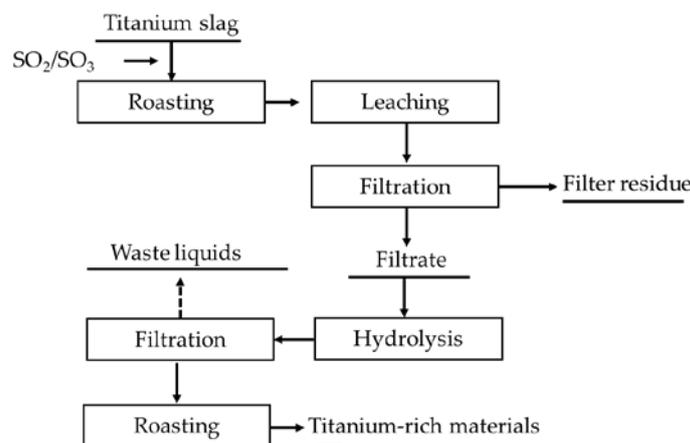
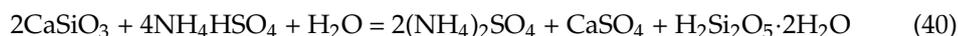
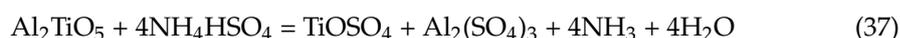
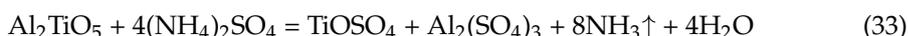


Figure 8. The diagram of the sulfur roasting leaching process.

Fouad [52] upgraded the low-grade titanium slag produced using the sulfation roasting technique. The final residue after leaching contained mostly kennedyite, rutile phases, and free silica (SiO_2) with traces of the calcium silicate phase ($\text{CaO} \cdot \text{SiO}_2$). Unfortunately, the removal rates of calcium, magnesium, and iron were only 80%, 37%, and 20%, respectively, for the sample treated at 800°C for 60 min.

Sui [50] used sulfur acid in place of the SO_2 gas to extract titanium from titanium slag. The acidolysis rate of TiO_2 was found to be above 96% under ideal conditions, which included a roasting time of 75 min, a roasting temperature of 310°C , a mass ratio of acid to ore of 2:1, and a particle size of 45–53 μm . Sui [53] also studied the reaction kinetics of roasting high-titanium slag with concentrated sulfuric acid, finding that the roasting kinetics were best fitted to a shrinking core model, with the reaction rate controlled by internal diffusion on the solid product layer. The roasting reaction has an

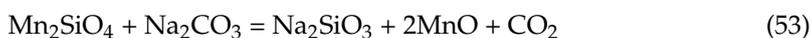
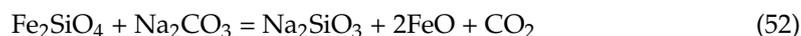
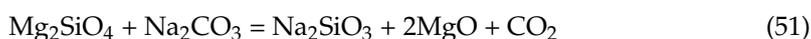
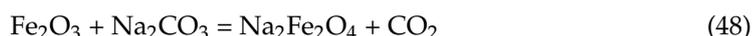
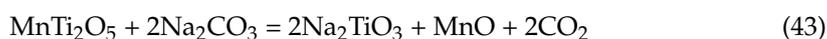
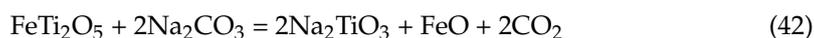
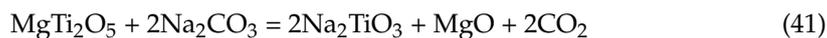
apparent activation energy of 18.94 kJ/mol, which is consistent with a variety of diffusion-controlled processes.

Recently, Zhang et al. [54] suggested an ammonium sulfate roasting method for simultaneous Ti and Al recovery, in which 91.7% of the titanium and 97% of the aluminum were extracted. Large amounts of ammonium hydroxide and acidic leaching waste comprising calcium sulfate and silicon dioxide, on the other hand, were discharged, and these are difficult to use. After roasting at a mass ratio of 2:1 for ammonium sulfate (AS) to titanium slag and at 350 °C for 2 h, Wang [55] found that the sulfation ratios of calcium, magnesium, titanium, and aluminum reached 92.6%, 87%, and 84.4%, respectively. Bian [56] also found that the titanium, aluminum, and magnesium extraction rates were 94.5%, 91.9%, and 97.4%, respectively, after pressure roasting at an As-to-slag mass ratio of 3:1 at 370 °C for 90 min.

In summary, sulfur roasting–leaching obtained desirable results for extracting titanium from titanium slag. Unfortunately, a large amount of sulfate needs to be added externally, the sulfide produced during the roasting process is difficult to handle, and the process has strict equipment requirements; the process has not been reported industrially.

3.2.2. Alkaline Roasting–Leaching Process

Alkaline roasting is used to reconstitute the high-temperature mineral phase of titanium slag by adding alkali or alkali salts at high temperatures to form water-soluble titanates, which are subsequently separated from impurity elements through leaching. The chemical reactions that may occur during the roasting process are shown below:



The alkaline roasting–leaching process has been deemed a promising method for titanium cleaner production in molten salt [57,58]. From this point of view, an alkaline roasting–leaching process has also been established to treat titanium slag [11,59,60]. The process is based on phase reconstruction at high temperatures by adding alkaline solutions. In this process, titanium can be extracted by forming titanate under alkaline conditions, and titanate can be easily separated from titanium slag. Xue and Wang et al. [61,62] proposed decomposing titanium slag in a NaOH molten-salt medium at atmospheric pressure to produce TiO₂ powder. Under ideal conditions of a temperature of 475 °C, a NaOH-to-slag mass ratio of 1.5:1, and 48–58 μm, around 95–98% of titanium in the titanium slag could be recovered. Meng [63] proceeded to investigate whether about 99% of titanium in the low-grade Ti slag could be decomposed at a loosening extent of roasting products of >90% in 4 wt% KMnO₄ as an anticaking additive.

According to Jarish [64], Na_2CO_3 and NaHCO_3 can be used to replace alkaline conditions for upgrading titanium slag. Dong [11,65] reported that rutile assaying of over 95% TiO_2 and 0.82% $\text{MgO} + \text{CaO}$ was obtained under optimized roasting conditions using a Na_2CO_3 -to-slag weight ratio of 3:7 at 850°C – 900°C for 1 h. Peng [19,66] demonstrated that the anosovite phase in slags was converted into rutile TiO_2 and that the valence of titanium was also increased as a result of the treatment. It was possible to remove nearly all of the titanium in the titanium slag. A schematic diagram of the reaction mechanism in the titanium slag is shown in Figure 9.

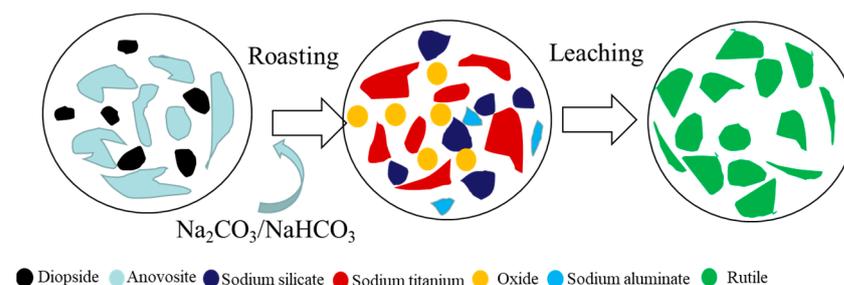
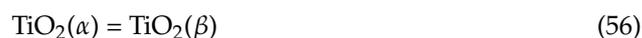
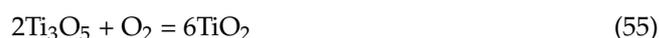


Figure 9. Schematic diagram of the reaction mechanism in titanium slag using alkaline roasting.

The extraction of titanium from titanium slag through alkaline roasting produces a good outcome, but the excessive addition of sodomizing agents during the alkaline roasting process can cause severe erosion of the reacting furnace lining. Acid leaching can cause serious corrosion to leaching equipment. Therefore, the entire alkaline roasting leaching process involves the erosion of the equipment, which needs to be made more resistant to corrosion and incredibly high-temperature erosion.

3.2.3. Oxide Roasting–Leaching Process

The oxide roasting–leaching process is a phase transformation process for synthesizing rutile from titanium slag. At high temperatures, oxidation roasting converts the black titanite in titanium slag into a stable rutile phase. The stable rutile cannot be dissolved by acids or alkalis, whereas acids or alkalis can dissolve the partially converted black titanite and silicate phases for separation from the titanium. The main reactions of oxide roasting are shown as follows:



This process was first developed by Leddy [67] in the United States. The process was first used to upgrade high titanium slag in 1962 and the results show that the titanium slag can be upgraded from 70% to 90%. In the process, $\text{M}_x\text{Ti}_{3-x}\text{O}_5$ ($0 < x < 2$, $\text{M} = \text{Ti, Fe, Al, Mg, etc.}$) was transformed to rutile, which had a stable structure, and leaching removed it from the other phase. The key to this process is phase transformation.

Leaching slag following heat treatment, according to Samal et al. [68], could increase the quality of synthetic rutile. A titaniferous intermediate product is produced after heat treatment, including the rutile and pseudobrookite phases. Oxide roasting–leaching is an effective method for transforming $M_xTi_{3-x}O_5$ ($0 < x < 2$, $M = Ti, Fe, Al, Mg$, etc.).

Liu [69] analyzed the thermodynamic behavior of titanium slag during oxide roasting. The results indicated that rutile and M_3O_5 solid solutions were formed by the oxidation of titanium and iron with lower valences in the calcination process. Ji [70] examined the FeO - Fe_2O_3 - TiO_2 phase diagram and found that at 1256 °C, Fe_2O_3 , TiO_2 , and spinel can form a solid solution, which is the correct explanation for Fe and Ti separation problems at 1250 °C. A solid solution of Fe_2TiO_5 , $FeTiO_3$, and spinel formed when the temperature hit 1266 °C. The solid solution of $FeTiO_3$ - FeO -ulvospinel was formed as the temperature increased to 1270–1300 °C, preventing further oxidation of FeO during the high-temperature roasting process. Zheng and Jing [71,72] further investigated the transformation behavior of titanium slag during the oxidation roasting process. The microstructure and element distribution of the mineral phase in the oxidized titanium slag were dramatically changed by high temperatures according to these findings. Rutile has a transformation rate of 68.79%. At the same time, the oxidation process of titanium slag is described in Figure 10.

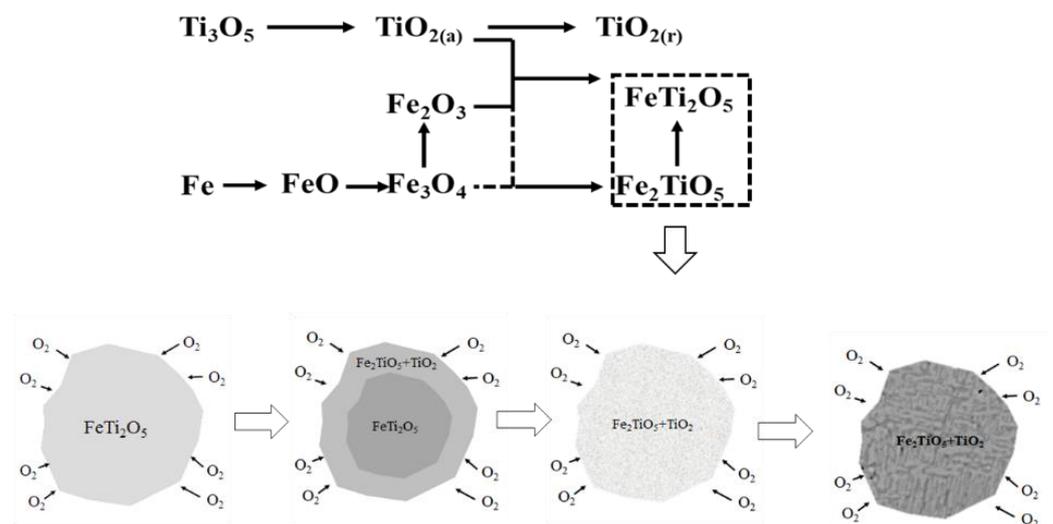


Figure 10. The oxidation process of anovosite in titanium slag.

Recently, Peng et al. [73,74] proposed microwave heating to upgrade titanium slag. The microwave perturbation technique is based on a change in resonant frequency in the resonant cavity and a drop in the microwave cavity's quality factor. Their results show that iron titanium oxide can be partially transformed into Ti_2O_3 in high titanium slag during mechanical activation and can be used to produce synthetic rutile under microwave heating. Chen [75] reported that the anovosite phase in titanium slag was transformed into synthetic rutile with a microwave heating temperature of 950 °C and 60 min. Figure 11 shows microstructure images of the titanium slag before and after microwave heating. Contrasting Figure 11a, b, it can be found that the surface structures of the primary particles have a tighter and smoother surface morphology, with more small pits and striations emerging on the titania slag surface, whereas the microwave-treated samples seem uneven, with a complex acicular structure. Microwave irradiation may have expanded the pores on the sample surface, resulting in an increase in surface area. However, the process of microwave heat faces a serious problem of facility upsizing.

The oxide roasting–leaching process has excellent prospects for extracting titanium slag. With no need to add other reagents and heat resources, the process can use waste heat after ilmenite electric furnace smelting.

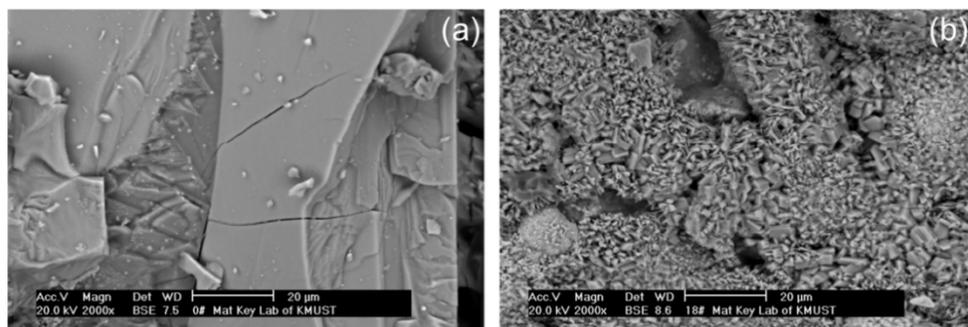


Figure 11. The microstructure images of titanium slag before and after microwave heating; (a) the titanium slag untreated; (b) Titanium roasted by microwave heating [75].

3.2.4. Oxidation and Reduction Roasting–Leaching Process

The titanium slag is modified through high-temperature oxidation roasting, resulting in a change in the structure of the slag, making it loose and porous, and then it is subjected to reduction treatment, where the porous structure of the slag aids in the contact with the reducing gas and strengthens the slag’s reducing effect. Finally, acid leaching is used to upgrade the reduced slag to produce a high-quality titanium-rich material. The flow diagram of the oxidation and reduction roasting–leaching process is shown in Figure 12. The chemical reactions that may occur during the roasting process are shown below:

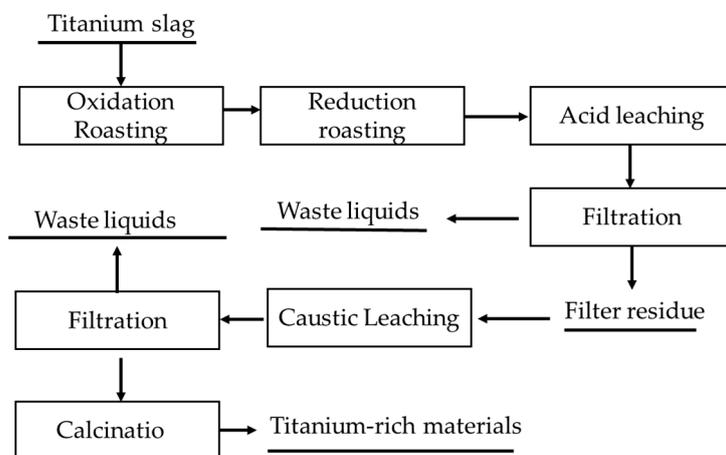
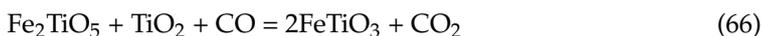


Figure 12. The diagram of the oxidation and reduction roasting–leaching process.

Krzysztof invented a reduction leaching procedure to extract titanium from titanium slag with oxides [14]. This method has the benefit of being able to create a high TiO₂ content product suited for the chloride process of TiO₂ pigment products. The critical consideration of the process, according to Fang et al. [76], is that it starts with a low-cost precursor (UGS) and uses the least expensive reductant (Mg); the TiH₂ formed after reduction, which chemically separates Ti from other impurities, allows for impurity removal via chemical leaching.

Lasheen [77] first presented the mechanism of the process of thermal oxidation and reduction in a controlled gas atmosphere to create leachable slag as appropriate for use as feed material in the chlorination process. The findings showed that the heating of a fully divided slag under oxidizing conditions allowed for a considerable proportion of iron in the ferric state Fe³⁺ and titanium species in the Ti⁴⁺ state, as well as an increase in the pseudobrookite

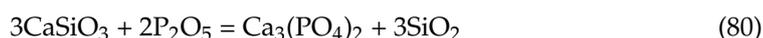
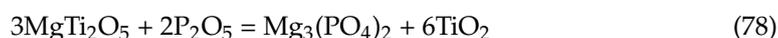
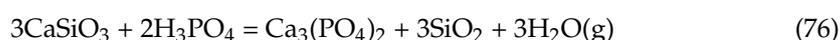
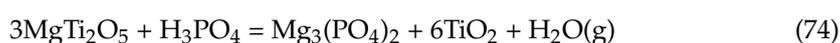
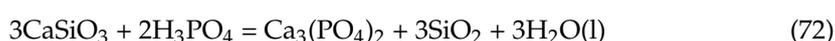
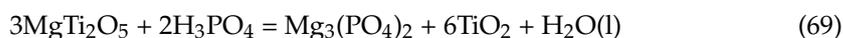
and rutile phases. Then, hydrogen gas was used at 800 °C for different periods to convert the significant portion of iron in the ferric state Fe^{3+} to the ferrous state Fe^{2+} .

According to Zhang [78,79], the reduction of $(\text{Fe}_2\text{TiO}_5)_a(\text{MgTi}_2\text{O}_5)_b$ resulted in the creation of intermediate $(\text{FeTi}_2\text{O}_5)_e(\text{MgTi}_2\text{O}_5)_f$ in the same M_3O_5 type, which then disintegrated further into the M_2O_3 phase. The a/b ratio had only a minor impact on the reduction of Fe^{3+} to Fe^{2+} but it had a significant impact on the phase transformation. Xie [80] investigated the reduction behavior of pre-oxidized titanium slag. The results showed that a relatively higher reduction rate of iron oxides with an airflow rate of 700 L/h and a temperature of 1000 °C for 2.5 h, and a cooling rate of 5 °C/h for reducing pre-oxidized titanium slag could be obtained. The slag phase was partially damaged, with a significantly high leaching rate of impurities, satisfying the requirements of rich titanium material for titanium dioxide production through a chlorination process.

Extracting titanium from titanium slag through oxidizing and reducing roasting–leaching was a unique commercial process at QIT. Unfortunately, the process used in Panzhihua titanium slag does not meet the chloride process requirements.

3.2.5. Phosphorylation Roasting–Leaching Process

In the phosphorylation roasting–leaching process, a certain amount of phosphoric acid is combined with titanium slag before being roasted at high temperatures. The impurity elements react with them to form water-soluble phosphate during the high-temperature phosphoric roasting process, and titanium is enriched in the rutile phase. Following the completion of the reaction, the rutile and impurity phosphate are separated through leaching to produce high-quality titanium-rich material. The chemical reactions that may occur during the roasting process are shown below:



The United States Bureau of Mines devised the phosphorylation roasting–leaching technique in the 1970s [81], and it is essentially a modified version of the normal thermal reduction process that can potentially solve the concerns outlined. This process obtains approximately more than 94% TiO_2 , and impurities can be removed with high efficiency.

Li [82] investigated the behavior of titanium slag activated using the phosphate process. The results showed that the methods were suitable for titanium slag. The titanium-bearing phase of titanium slag was oxidized in the presence of phosphorus, resulting in distinct rutile crystals and a glass phase. Leaching with dilute acid separated the rutile from the glassy impurities. Fe, Mg, Ca, and Al can also be efficiently removed through leaching, with 20 wt.% HCl at a liquid-to-solid ratio of 5:1 at 110 °C for 2 h, according to Liu [83,84]. It was

discovered that a NaOH leaching step is required to remove Si and P from synthetic rutile with a purity of 95.34% TiO₂ and 0.37% (MgO + CaO). Zheng [47] analyzed the mechanism for removing Mg and Ca from titanium slag using the phosphate process. The findings suggest that H₃PO₄ may aid in the breakdown of MgTi₂O₅ and CaSiO₃. The titanium-bearing mineral was converted to rutile, which enhanced the impurities in M_xTi_{3-x}O₅ into phosphate, which could be used in an acid leaching procedure. The phosphate process caused the transformation rate of rutile to increase from 67.8% to 80%. Figure 13 shows microstructure pictures of titanium slag before and after the phosphate process. The mechanism of the phosphate process is described in Figure 14.

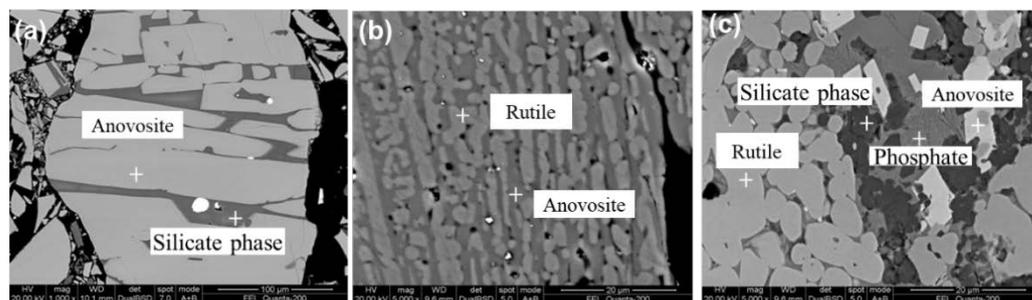


Figure 13. Microstructure images of titanium slag before and after the phosphate process: (a) titanium slag; (b) oxidation roasting at 1200°C; (c) 16% H₃PO₄ and oxidation roasting at 1200 °C [47].

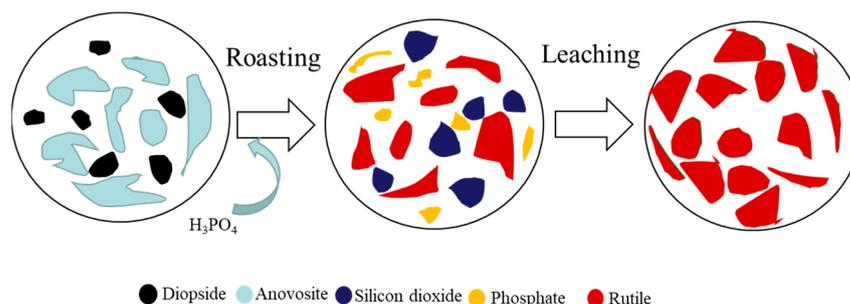


Figure 14. The mechanism of titanium slag handled using the phosphate process.

Chen [85,86] recently investigated how union phosphate and microwave heating processes affected the behavior of titanium slag. More than 97% TiO₂ and 0.26% (MgO + CaO) were extracted. When compared to the standard phosphate process, the transformation rate of rutile increased to 85%. In summary, upgrading titanium slag through the phosphate process can quickly meet the requirements of chloride products. The key to this process is selectively enriching titanium into rutile and impurities enriched in the glass phase with the best separation effect. Unfortunately, the number of phosphorylation additives causes severe environmental pollution and a high recovery cost.

3.3. The Effect of Impurities on the Utilisation of Titanium Slag

For titanium slag, whether it is for the preparation of titanium dioxide or of high-quality titanium-rich materials, the key to the process is the removal of impurities. To prepare titanium dioxide, the best white pigment from the titanium slag and impurities in the slag that affect the color system must be removed. High-quality titanium-rich materials are mainly used to prepare titanium tetrachloride TiCl₄. The chloride process has caveats, such as a sensitivity toward the presence of calcium and magnesium. CaCl₂ and MgCl₂ are non-volatile under the conditions of the chlorination reaction, and these chemicals tend to distort and agglutinate the reaction bed. In order to clearly demonstrate the influence of impurities on the utilization of titanium slag, Table 5 shows the direction of impurity elements and the effects on the products.

Table 5. The direction of impurity elements and the effects on the products.

Methods	Titanium-Containing Phases	Impurity Phase	Ref
H ₂ SO ₄ leaching	TiOSO ₄ , H ₂ TiO ₃ , TiO ₂	Fe ₂ (SO ₄) ₃ , MgSO ₄ , CaSO ₄ , Al ₂ (SO ₄) ₃ , H ₂ SiO ₃	[29]
HCl leaching	TiOCl ₂ , H ₂ TiO ₃ , TiO ₂	FeCl ₃ , MgCl ₂ , AlCl ₃ , CaCl ₂ , H ₂ SiO ₃	[34]
Fluoride leaching	(NH ₄) ₂ TiF ₆ , (NH ₄) ₃ TiO ₂ F ₅ , TiO ₂ , TiOF ₂	(NH ₄) ₂ SiF ₆ , (NH ₄) ₂ FeF ₆ , CaF ₂ , CaMg ₂ Al ₂ F ₁₂ , NH ₄ MgAlF ₆	[41]
Ammonia decomposition leaching	(NH ₄) ₂ TiO ₃ , TiO ₂	Fe(OH) ₃ , Mg(OH) ₂ , Ca(OH) ₂ , Al(OH) ₃	[25]
Sulfur roasting–leaching	TiOSO ₄ , H ₂ TiO ₃ , TiO ₂	Fe ₂ (SO ₄) ₃ , MgSO ₄ , CaSO ₄ , Al ₂ (SO ₄) ₃ , H ₂ SiO ₃	[53]
Alkaline roasting–leaching	Na ₂ TiO ₃ , TiO ₂	Na ₂ SiO ₃ , NaAlO ₂ , CaO, MgO, FeO	[11,65]
Oxide roasting–leaching	TiO ₂ , M _x Ti _{3–x} O ₅ (0 < x < 2, M = Ti, Fe, Al, Mg, etc.)	Fe ₂ (SO ₄) ₃ , MgSO ₄ , CaSO ₄ , Al ₂ (SO ₄) ₃ , FeCl ₃ , MgCl ₂ , AlCl ₃ , CaCl ₂ , H ₂ SiO ₃	[72]
Oxidation and reduction roasting–leaching	TiO ₂ , M _x Ti _{3–x} O ₅ (0 < x < 2, M = Ti, Fe, Al, Mg, etc.)	Fe ₂ (SO ₄) ₃ , MgSO ₄ , CaSO ₄ , Al ₂ (SO ₄) ₃ , FeCl ₃ , MgCl ₂ , AlCl ₃ , CaCl ₂ , H ₂ SiO ₃	[77]
Phosphorylation roasting–leaching	TiO ₂	Mg ₃ (PO ₄) ₂ , FePO ₄ , AlPO ₄ , Ca ₃ (PO ₄) ₂ , SiO ₂	[83,84]

4. Conclusions and Recommendations

Titanium slags produced during ilmenite electric furnace smelting contain 60–80% TiO₂, a crucial titanium resource in the titanium industry. Many processes are used to upgrade titanium slag to produce synthetic rutile. Most of these processes involve a combination of the technologies of modification and leaching and are expensive.

Leaching separation techniques with a simple process are widely used for extracting titanium from titanium slag. However, the extraction rate of titanium via these methods is shallow due to the complex mineralogical composition of the slags. The process of sulfur roasting–leaching has a desirable result for extracting titanium from titanium slag, but it also causes severe environmental pollution because of its SO₃ or SO₂ gases. The alkaline roasting–leaching process can effectively extract titanium from titanium slag, but the excessive addition of alkaline is expensive, and the equipment faces strict requirements. The oxidation and reduction roasting–leaching process was a unique commercial process for QIT. However, the titanium slag in Panzhihua cannot be handled due to high calcium and magnesium. In fact, several experiments conducted by the application of QIT process on Panzhihua slag were able to obtain only a titanium-rich feed with 89.8% TiO₂ and 0.5% and 0.6% CaO and MgO, which did not meet the requirements of the boiling chlorination charge. This is because the Panzhihua titanium resource is a high Ca–Mg titanium resource and the rutile phase transition during QIT oxidation and reduction is incomplete. The phosphate process can quickly meet the requirements of the chloride process; however, the number of phosphorylation additives brings with it severe environmental pollution and a high recovery cost. With fewer studies investigating the mechanism of ammonium hydroxide decomposition, ammonia hydroxide is a volatile reagent that causes severe environmental pollution and involves strict equipment requirements. The oxide roasting–leaching process can effectively extract titanium from titanium slag compared to these methods. With no need to add other reagents and heat resources, the process can use waste heat after ilmenite electric furnace smelting.

Overall, the oxide roasting–leaching process is more suitable for selectively extracting titanium from titanium slag, and leached solution can be used as a feedstock for sulfuric acid processing. This review is expected to serve as a helpful guide for promoting the treatment of titanium slags because the extraction of titanium from titanium slags through oxide roasting–leaching is recommended.

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and L.Y.; visualization and supervision, Y.G. and G.Q. All authors have read and agreed to the published version of the manuscript.

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