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A Clean Process to Prepare High-Quality Acid-Soluble Titanium Slag from Titanium Middling Ore

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Abstract: A direct reduction-magnetic separation-alkali leaching-dilute acid washing method was proposed to prepare high-quality acid-soluble titanium slag (HQASTS) from titanium middling ore. The relevant potential pH diagrams were built, and the analysis results showed that the pH values for alkali leaching and dilute acid washing should be higher than 13.50 and lower than 1.00, respectively. Increasing temperature was beneficial to alkali leaching but not to dilute acid washing. The effects of operating parameters on the TiO₂ content and impurity oxides extraction ratios of titanium slag were investigated, and the optimal experimental conditions were obtained. The HQASTS was obtained with TiO₂ and Fe₂O₃ content of 75.37 wt % and 0.96 wt %, respectively, under the above conditions. Furthermore, the leaching mechanism was studied by chemical analysis and X-ray diffraction (XRD) technology, and it was found that the alkali leaching-dilute acid washing process presented in this work could avoid the encapsulation of the unreacted anorthite by the calcium aluminum spinel generated in alkali leaching.

Keywords: potential pH diagram; high-quality acid-soluble titanium slag; titanium middling ore; alkali leaching; dilute acid washing; leaching mechanism

1. Introduction

Titanium dioxide pigment has many practical applications, such as paints, plastics, and paper-making plants [1–4]. At present, chloride and sulfate processes serve as the two main commercial strategies in the titanium dioxide industry [5,6]. The chloride process, which utilizes rutile as a raw material presently is more favorable economically and generates less waste products; however, sources of natural rutile are limited. Thus, a number of investigations [7–17] (as shown in Table S1 of Supplementary Materials) have been performed to prepare synthetic rutile. The sulfate process that uses ilmenite or acid soluble titanium slag as raw materials is widely applied, but it is lengthy, and ferrous sulfate byproduct is less marketable. These problems are caused by the high content of impurities in the raw materials. It is well known that iron is the most abundant impurity in ilmenite and acid soluble titanium slag and their contents are ~35 wt % and ~10 wt %, respectively. This part of the iron element eventually enters titaniferous solution in the form of ferrous sulfate. This not only adds the processes of the freezing crystallization and separation of copperas but also produces a large amount of ferrous sulfate. In addition, the high content of ferrous sulfate in titaniferous solution will increase the workload for the purification of metatitanic acid. Thus, it is very meaningful to produce high-quality acid-soluble titanium slag (HQASTS) with low iron content for the sulfate process.

At present, titanium middling ore has been mainly used as the protective material of the blast furnace owing to low TiO₂ content (TiO₂ < 40 wt %), and its comprehensive utilization value is

relatively low. In order to solve this problem, a method for direct reduction-magnetic separation-alkali leaching-dilute acid (HCl concentration ≤ 1.29 mol/L) washing was proposed in this work to prepare the HASTS, using titanium middling ore as feedstock. The feasibility of the alkali leaching-dilute acid washing process was evaluated by means of thermodynamic analysis. According to the relevant investigations [18–24], binary potential pH diagrams for Si-H₂O, Al-H₂O, Mg-H₂O, V-H₂O, Ca-H₂O, Fe-H₂O and Mn-H₂O systems have been reported. It was found that Al₂O₃, MgO, V₂O₅, VO₂, CaO, FeO and MnO could be leached by dilute acid, and SiO₂ could be leached by alkali. As titanium slag contains a certain amount of FeTiO₃, CaTiO₃, etc., it is necessary to draw ternary potential pH diagrams for Ca-Ti-H₂O, Fe-Ti-H₂O, Mn-Ti-H₂O Al-Ti-H₂O, Mg-Ti-H₂O and V-Ti-H₂O systems. The ternary potential pH diagram of Si-Ti-H₂O systems cannot be drawn because there are no silicon data in the FactSage software database.

The objective of this study is to prepare high-quality acid-soluble titanium slag by a direct reduction-magnetic separation-alkali leaching-dilute acid washing method and simultaneously realize the comprehensive utilization of titanium middling ore. For optimizing leaching conditions, the effects of operating parameters on TiO₂ content and impurity oxides extraction ratios in the titanium slag were investigated. In order to understand the leaching mechanism, the chemical and phase compositions of low-grade titanium slag, the cake after alkali leaching and the cake after alkali leaching-dilute acid washing were determined by chemical analysis and XRD technology.

2. Materials and Methods

In this work, titanium middling ore was obtained from the Panzhihua Iron and Steel Research Institute (Sichuan Province, China). The iron element in the titanium middling ore was removed by the pretreatment of the direct reduction-magnetic separation to obtain low-grade titanium slag. The HASTS from low-grade titanium slag was produced via an alkali leaching-dilute acid washing process.

The content of each element was measured using chemical analysis according to Chinese standards. Such as GB/T 14506.8-2010 for Ti, GB/T 6730.65-2009 for Fe, GB/T 6730.10-2014 for Si etc. The X-ray diffraction (XRD, X' Pert Pro; PANalytical, Almelo, The Netherlands) with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV, 40 mA) was employed to characterize the phases. The thermodynamic analysis of the experiment was performed using E-pH module of the FactSage 7.1. Distilled water was used as a solvent throughout the experiment. Other chemical agents used in the present work were provided by China National Medicines Corporation Ltd, Shenyang, China. They are of analytical grade and were used as received. The X-ray diffraction pattern of titanium middling ore is shown in Figure 1. The chemical compositions of titanium middling ore and low-grade titanium slag are listed in Table 1. The schematic diagram of the experimental process is shown in Figure 2.

Figure 1. The X-ray diffraction pattern of titanium middling ore.

Table 1. Chemical compositions of samples (wt %) (1: titanium middling ore; 2: low-grade titanium slag).

Sample	TiO ₂	Fe ₂ O ₃	SiO ₂	CaO	Al ₂ O ₃	V ₂ O ₅	MgO	MnO	Na ₂ O
1	37.94	38.12	9.61	5.13	3.69	2.11	1.15	0.56	0.15
2	60.00	2.49	15.27	8.12	5.91	3.46	1.87	0.91	0.23

Figure 2. Schematic diagram of the experimental process in the present work. High-quality acid-soluble titanium slag (HQASTS).

As shown in Figure 2, the mixtures (titanium middling ore and 12 wt % anthracite) were reduced at a temperature of 1350 °C for 30 min in a resistance furnace. Next, the reduction product was grinded in a rod mill and then processed through a magnetic separator with a magnetic field intensity of 120 mT. The direct reduction and magnetic separation experiments were carried out in a vertical MoSi₂ resistance furnace and a Davies Magnetic Tube (CXG-Φ50, China Tangshan Shida Automation Instrument Technology Co., Ltd, Tangshan, China), respectively.

Before alkali leaching, the low-grade titanium slag was ground to a particle size of less than 48 µm and dried in an oven at 110 °C for 24 h. The leaching experiments were performed at atmospheric pressure in a 500 mL three-necked flask equipped with a reflux condenser. The reaction mixture was heated by a thermostatic water bath and agitated by a magnetic stirrer at a stirring ratio of 500 rpm.

For the alkali leaching process, the amount of titanium slag was fixed at 20 g. According to a certain L/S, the volume of alkali leaching solution can be determined. Then, a known concentration of NaOH solution was taken and poured into a three-necked flask. Once the specified temperature was reached, titanium slag was added to the reactor and leached for a certain time. At the end of the run, the slurry was filtered to separate the cake from the alkaline solution. The cake was washed with distilled water, dried in an oven at 110 °C for 24 h, and submitted for chemical analysis.

Before dilute acid washing, titanium slag was first leached under the above optimal alkali leaching conditions. Then, the production of alkali leaching was washed by dilute acid (HCl). The experimental

procedure is the same as the alkaline leaching experiment. The waste acid and alkaline solutions produced in the process can be treated by neutralization.

3. Results and Discussion

3.1. Thermodynamic Analysis

To understand the solving behavior of metal elements in the process of alkali leaching-dilute acid washing, ternary potential-pH diagrams were drawn. The results are shown in Figures 3–8. The molarity concentration used for the calculation is 1 mol/L.

Figure 3. Potential-pH diagrams for Al-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

Figure 4. Potential-pH diagrams for Mg-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

Figure 5. Potential-pH diagrams for V-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

Figure 6. Potential-pH diagrams for Ca-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

Figure 7. Potential-pH diagrams for Fe-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

Figure 8. Potential-pH diagrams for Mn-Ti-H₂O systems: (a) 25 °C; (b) 100 °C.

As can be seen from Figures 3–5, Al₂O₃, MgO and VO₂ in low-grade titanium slag can be removed by dilute acid as Al³⁺, Mg²⁺ and VO²⁺, respectively, whereas titanium is still present as oxide. When the temperature increases to 100 °C, Al₂O₃ can be leached by alkali with a minimum pH 13.50, indicating that the alkaline leaching of Al₂O₃ can be achieved through increasing the temperature. The V₂O₅ can also be leached by alkali in the form of HVO₄^{2−}, whereas V₂O₃ and VO cannot be leached by acid or alkali. Additionally, as the temperature rises from 25 to 100 °C, the stable areas of Al³⁺, Mg²⁺ and VO²⁺ decrease, whereas those AlO₂[−] and HVO₄^{2−} increase, suggesting that increasing temperature not only reduces the required pH values of the dilute acid washing of Al₂O₃, MgO and VO₂ but also decreases the required pH values of the alkali leaching of Al₂O₃ and VO₅.

As shown in Figures 6–8, CaTiO_3 , FeTiO_3 and MnTiO_3 can be removed by dilute acid in the form of Ca^{2+} , Fe^{2+} and Mn^{2+} , whereas titanium still exists as oxide. It is worth noting that Fe(III) cannot be removed by dilute acid due to the not sufficient low pH of the acid solution. However, Fe(II) can be more easily removed by dilute acid. Therefore, reducing Fe(III) into Fe(II) or metallic iron can significantly enhance the acid solubility of ferrous components in the titanium slag. In addition, with temperature increasing, the stable areas of Ca^{2+} , Fe^{2+} and Mn^{2+} decrease sharply, which means that increasing temperature can reduce the required pH values of the dilute acid washing of CaTiO_3 , FeTiO_3 and MnTiO_3 .

The above analysis indicates that the alkali leaching-dilute acid washing process for upgrading low-grade titanium slag is theoretically feasible. The pH of the alkali leaching should be higher than 13.50 (Figure 3, Al-Ti- H_2O , 100 °C) and the pH of the dilute acid washing should be lower than 1.00 (Figure 5, V-Ti- H_2O , 100 °C). A higher temperature is conducive to alkali leaching, but the trend for dilute acid washing is the opposite. Thus, the temperatures for alkali leaching and dilute acid washing can be set at 100 °C and 25 °C, respectively. This can dramatically decrease the NaOH concentration of the alkali leaching and the HCl concentration of the dilute acid washing, which means that a large amount of acid and alkali can be saved.

3.2. Alkali Leaching

According to the relevant literature [24] and Figure 3, it can be seen that SiO_2 and Al_2O_3 in the slag can be theoretically leached by alkali. Thus, the TiO_2 content in the slag, SiO_2 extraction ratio and Al_2O_3 extraction ratio were determined by chemical analysis. The results are shown in Figure 9. The experimental program of the alkali leaching is provided in Table 2. The SiO_2 (G) and Al_2O_3 (H) extraction ratios were calculated using the following Equations (1) and (2):

$$G = \frac{m_0 \times w_{G0} - m_1 \times w_{G1}}{m_0 \times w_{G0}} \quad (1)$$

$$H = \frac{m_0 \times w_{H0} - m_1 \times w_{H1}}{m_0 \times w_{H0}} \quad (2)$$

where m_0 is the mass of low-grade titanium slag (20 g), m_1 is the mass of the cake after alkali leaching (g), w_{G0} and w_{H0} are the SiO_2 and Al_2O_3 content, respectively, of low-grade titanium slag (wt %), and w_{G1} and w_{H1} are the SiO_2 and Al_2O_3 content, respectively, of the cake after alkali leaching (wt %).

Table 2. Experimental program of alkali leaching.

No.	Fixed Conditions	Variable	Optimal Value
a	L/S 4, Temperature 55 °C, Time 60 min	NaOH concentration (mol/L): 1.6, 2.2, 2.8, 3.4, 4.1, 4.8, 5.5, 6.3	2.8
b	NaOH concentration 2.8 mol/L, Temperature 55 °C, Time 60 min	L/S (mL/g): 2, 4, 6, 8, 10, 12, 14, 16	4
c	NaOH concentration 2.8 mol/L, L/S 4, Time 60 min	Temperature (°C): 25, 35, 45, 55, 65, 75, 85, 95	95
d	NaOH concentration 2.8 mol/L, L/S 4, Temperature 95 °C	Time (min): 30, 60, 90, 120, 150, 180, 210, 240	60

The effect of NaOH concentration on TiO_2 content is delineated in Figure 9a. The TiO_2 content increased rapidly from 61.62 to 64.58 wt % as NaOH concentration increased from 1.6 to 2.8 mol/L. Within a NaOH concentration range of 2.8–4.8 mol/L, TiO_2 content increased slowly. When NaOH concentration was higher than 4.8 mol/L, the TiO_2 content remained unchanged. Thus, a NaOH concentration of 2.8 mol/L was used in the following experiments. It can be seen that SiO_2 in the slag can be leached by alkali and Al_2O_3 cannot be removed by alkali under the above conditions.

Figure 9. Effects of NaOH concentration (a), liquid/solid ratio (b), temperature (c) and time (d) on TiO₂ content, G (SiO₂ extraction ratio) and H (Al₂O₃ extraction ratio).

The effect of liquid/solid ratio (L/S) on TiO₂ content is illustrated in Figure 9b. It was found that TiO₂ content increased markedly when L/S increased from 2 to 4. As L/S increased from 4 to 10, TiO₂ content increased insignificantly. At L/S > 10, TiO₂ content remained unchanged. Thus, a L/S of 4 was used in subsequent experiments. As shown in Figure 9b, the variation tendency of SiO₂ extraction ratio was consistent with that of TiO₂ content, whereas the Al₂O₃ extraction ratio remained 0 wt %. This means that only part of SiO₂ was leached under the aforementioned conditions.

Figure 9c shows the effect of temperature on TiO₂ content. It is obvious that TiO₂ content monotonically increased with the rise in temperature. Therefore, the optimum temperature was 95 °C. When temperature was more than 75 °C, the SiO₂ extraction rate remained unchanged, but the TiO₂

content continued to increase. This is because Al_2O_3 started to be leached by a 2.8 mol/L NaOH solution (pH 14.44) at 75 °C. This also confirmed the previous conclusion (Figure 3) that increasing temperature can achieve the alkali leaching of Al_2O_3 .

Figure 9d illustrates the effect of time on TiO_2 content. When time increased from 30 min to 60 min, TiO_2 content rapidly increased. As time continued to increase to 90 min, TiO_2 content increased slightly. This is because both SiO_2 and Al_2O_3 can be leached before 30 min, and only a small quantity of SiO_2 was leached after 30 min. Hence, the optimum time was 60 min.

Taking the above results into consideration, the optimal alkali-leaching conditions were as follows: NaOH concentration 2.8 mol/L (pH 14.44), L/S 4, temperature 95 °C and time 60 min. The TiO_2 content of the titanium slag, SiO_2 extraction ratio and Al_2O_3 extraction ratio were 65.83 wt %, 35.69 wt % and 15.06 wt %, respectively, which indicates single alkali leaching cannot effectively increase TiO_2 content in the slag. This may be because CaAl_2O_4 (calcium aluminum spinel) produced in the process of alkali leaching covers the surface of unreacted $\text{CaAl}_2(\text{SiO}_4)_2$ (anorthite) and prevents the reaction between NaOH and $\text{CaAl}_2(\text{SiO}_4)_2$. The reliability of potential-pH diagrams for Al-Ti- H_2O systems was confirmed by measuring the Al_2O_3 extraction ratio in the slag. Moreover, it was found that the extraction ratio of Al_2O_3 is much lower than that of SiO_2 . As shown in Figure 10, it can be explained by the fact that the standard Gibbs free energy change of chemical reactions (b) is much smaller than that of reaction (a), i.e., NaOH prefers to react with SiO_2 rather than Al_2O_3 . On the other hand, a small amount of insoluble $\text{NaAl}(\text{OH})_4$ was formed during the alkali-leaching process, resulting in a lower extraction rate of Al_2O_3 . The $\text{NaAl}(\text{OH})_4$ content can be determined by the sodium content of the cake after alkali leaching. As shown in Table 4, the Na_2O content of the cake increased after alkali leaching. Thus, the main reaction that occurred in the alkali-leaching process is as follows:

Figure 10. Standard Gibbs free energy change of reactions (a) and (b) at different temperatures.

3.3. Alkali Leaching-Dilute Acid Washing

In this work, the low-grade titanium slag was first leached by alkali under the above-mentioned optimal conditions before dilute acid washing. The experimental program of dilute acid washing is shown in Table 3. Based on Figures 3–8, it was observed that Al_2O_3 , MgO , VO_2 , CaO , FeO , Fe and MnO

in the slag can be theoretically leached by dilute acid. The MgO and MnO extraction ratios were not measured because MgO mainly exists in the form of the anosovite phase, which is insoluble in acid, and the MnO content is relatively low. Therefore, the TiO₂ content in the slag, CaO extraction ratio, Al₂O₃ extraction ratio, Fe₂O₃ extraction ratio (the total extraction ratio of various valence iron oxides) and V₂O₅ extraction ratio (the total extraction ratio of various valence vanadium oxides) were determined by chemical analysis during the dilute acid washing process. The results are presented in Figure 11. The calculation equations of CaO extraction ratio (B), Al₂O₃ extraction ratio (C), Fe₂O₃ extraction ratio (D) and V₂O₅ extraction ratio (E) were given in Equations (4), (5), (6) and (7), respectively:

$$B = \frac{m_0 \times w_{B0} - m_2 \times w_{B2}}{m_0 \times w_{B0}} \quad (4)$$

$$C = \frac{m_0 \times w_{C0} - m_2 \times w_{C2}}{m_0 \times w_{C0}} \quad (5)$$

$$D = \frac{m_0 \times w_{D0} - m_2 \times w_{D2}}{m_0 \times w_{D0}} \quad (6)$$

$$E = \frac{m_0 \times w_{E0} - m_2 \times w_{E2}}{m_0 \times w_{E0}} \quad (7)$$

where m_0 is the mass of low-grade titanium slag (20 g), m_2 is the mass of the cake after alkali leaching-dilute acid washing (g), w_{B0} , w_{C0} , w_{D0} and w_{E0} are the CaO, Al₂O₃, Fe₂O₃ and V₂O₅ content, respectively, of low-grade titanium slag (wt %) and w_{B2} , w_{C2} , w_{D2} and w_{E2} are the CaO, Al₂O₃, Fe₂O₃ and V₂O₅ content, respectively, of the cake after alkali leaching-dilute acid washing (wt %).

Table 3. Experimental program of dilute acid washing.

No.	Fixed Conditions	Variable	Optimal Value
a	L/S 6, Temperature 35 °C, Time 60 min	HCl concentration (mol/L): 0.28, 0.42, 0.56, 0.70, 0.85, 0.99, 1.14, 1.29	0.56
b	HCl concentration 0.56 mol/L, Temperature 35 °C, Time 60 min	L/S (mL/g): 3, 4, 5, 6, 7, 8, 9, 10	6
c	HCl concentration 0.56 mol/L, L/S 6, Time 60 min	Temperature (°C): 25, 30, 35, 40, 45, 50, 55, 60	45
d	HCl concentration 0.56 mol/L, L/S 6, Temperature 45 °C	Time (min): 30, 60, 90, 120, 150, 180, 210, 240	60

The effect of HCl concentration on TiO₂ content is shown in Figure 11a. The TiO₂ content sharply increased with HCl concentration increasing from 0.28 to 0.56 mol/L. Thereafter, in the HCl concentration range of 0.56–1.29 mol/L, the TiO₂ content continued to increase at a slow rate. This can be attributed to the fact that CaO, Al₂O₃, Fe₂O₃ and V₂O₅ extraction ratios increased significantly as HCl concentration increased from 0.28 to 0.56 mol/L, and then these extraction ratios increased slowly when the HCl concentration was more than 0.56 mol/L. Taking into account cleaner production and reducing cost, 0.56 mol/L HCl was chosen as the optimum concentration.

The effect of L/S on TiO₂ content is illustrated in Figure 11b. The TiO₂ content rapidly increased from 71.29 wt % with L/S 3 to 73.91 wt % with L/S 6. When L/S increases from 6 to 8, the TiO₂ content increased slowly. As for the case of L/S > 8, the TiO₂ content in the slag was almost constant. It can be explained by the fact that the variation tendencies of Al₂O₃, CaO, Fe₂O₃ and V₂O₅ extraction ratios were consistent with that of TiO₂ content. Thus, the optimum L/S was 6.

Figure 11c shows the effect of temperature on TiO₂ content. The TiO₂ content dramatically increased when temperature increased from 25 to 45 °C. Nevertheless, the TiO₂ content slightly increased in the temperature range of 45–60 °C. This is because CaO, Al₂O₃, Fe₂O₃ and V₂O₅ extraction ratios rapidly increased at 25–45 °C. When temperature was more than 45 °C, the extraction ratio of Fe₂O₃ remained unchanged and the extraction ratios of CaO and Al₂O₃ increased at a low ratio. Thus, the optimum temperature was 45 °C.

Figure 11d illustrates the effect of time on TiO₂ content. The TiO₂ content sharply increased as time increased from 30 to 60 min, and then slightly increased with more than 60 min leaching. This is because CaO, Al₂O₃, Fe₂O₃ and V₂O₅ can be removed at a high rate as the time increased from 30 to

60 min. When the time was longer than 60 min, the CaO, Al₂O₃ and V₂O₅ extraction ratios increased slightly and Fe₂O₃ extraction rate was almost constant. Hence, the optimum time was 60 min.

Figure 11. Effects of dilute acid (HCl) concentration (a), L/S ratio (b), temperature (c) and time (d) on *F* (TiO₂ content of slag), *E* (V₂O₅ extraction ratio), *D* (Fe₂O₃ extraction ratio), *C* (Al₂O₃ extraction ratio) and *B* (CaO extraction ratio).

In summary, the optimal dilute acid washing conditions were 0.56 mol/L HCl concentration (pH 0.26), L/S 6, temperature 45 °C and time 60 min. The TiO₂ content of the HQASTS, CaO extraction ratio, Al₂O₃ extraction ratio, Fe₂O₃ extraction ratio and V₂O₅ extraction ratio were 75.37 wt %, 47.57 wt %, 55.33 wt %, 60.49 wt % and 12.10 wt %, respectively; indicating that the process of alkaline leaching-dilute acid washing can significantly improve TiO₂ content in titanium-bearing materials.

In this present study, vanadium oxides in the low-grade titanium slag mainly consist of V_2O_3 and a small amount of VO_2 . It can be seen from Figure 5 that V_2O_3 cannot be removed by acid but VO_2 can. Therefore, only a small quantity of VO_2 was dissolved in acid solution. This is the reason why the V_2O_5 extraction rate is only 12.10 wt %. On the other hand, the reliability of potential-pH diagrams (Ca-Ti- H_2O , Al-Ti- H_2O , Fe-Ti- H_2O and V-Ti- H_2O) was confirmed by measuring the CaO, Al_2O_3 , Fe_2O_3 and V_2O_5 extraction ratios in the slag. In addition, as shown in Figure 11, the variation trends of the Al_2O_3 and CaO extraction ratios under the same conditions were very similar. It can be inferred that Al_2O_3 and CaO were leached in equal proportions. Thus, the main reaction that occurred in the dilute acid washing process is as follows:

3.4. Leaching Mechanism

In order to gain insight into the leaching mechanism of process, the chemical analysis of resulting solids and solutions as well as XRD test were performed. The results are shown in Tables 4 and 5 and Figure 12.

Table 4. Chemical compositions of residual solids (wt %) (1: low-grade titanium slag; 2: the cake after optimal alkali leaching; 3: the cake after optimal alkali leaching-dilute acid washing).

Sample	TiO ₂	SiO ₂	CaO	Al ₂ O ₃	V ₂ O ₅	Fe ₂ O ₃	MgO	MnO	Na ₂ O
1	60.00	15.27	8.12	5.91	3.46	2.49	1.87	0.91	0.23
2	65.83	9.82	8.24	5.02	3.47	2.43	2.01	0.95	0.95
3	75.37	8.85	4.32	2.64	3.05	0.96	2.02	0.68	0.18

Table 5. Chemical compositions of leaching solutions (g/L) (A: the solution after optimal alkali leaching; B: the solution after optimal dilute acid washing).

Sample	Ti	Si	Ca	Al	V	Fe	Mg	Mn
A	<0.1	20.8	<0.1	4.0	<0.1	<0.1	<0.1	<0.1
B	<0.1	0.6	6.3	3.8	0.9	2.2	<0.1	0.6

Figure 12. The X-ray diffraction (XRD) patterns of residual solids (1: low-grade titanium slag; 2: the cake after optimal alkali leaching; 3: the cake after optimal alkali leaching-dilute acid washing).

As seen from Tables 4 and 5, more than one-third of SiO_2 and a small amount of Al_2O_3 were dissolved in an alkaline solution. In the process of dilute acid washing, most of the Fe_2O_3 , Al_2O_3 , CaO and MnO and a small quantity of V_2O_5 were dissolved in acid solution. The results indicated that the main reactions that occurred in the alkali leaching and dilute acid washing were (3) and (8), respectively. Despite anosovite ($\text{Mg}_x\text{Ti}_{3-x}\text{O}_5$, $0 \leq x \leq 2$) phase is insoluble in acid, a small quantity of MgO must be dissolved because the solid mass decreased during the dilute acid washing process and the MgO content remained constant. Consequently, the mass of MgO decreased, indicating that some MgO exists in other phases. The experimental results are consistent with the previous analysis of potential-pH diagrams and also confirm their authenticity. Moreover, Table 5 shows that the Ti content of alkali and acid solutions is quite low, indicating that almost all Ti components in the slag can be recovered. It is remarkable that the Fe_2O_3 content of the HQASTS is only 0.96 wt %. This not only eliminates the processes of the freezing crystallization and separation copperas for sulfate process but also greatly reduces the workload of the subsequent purification of metatitanic acid.

As shown in Figure 12, $\text{CaAl}_2(\text{SiO}_4)_2$ (anorthite) was transformed into CaAl_2O_4 (calcium aluminum spinel) after alkali leaching, and CaAl_2O_4 disappeared after dilute acid washing. It was found from experimental results of Sections 3.2 and 3.3 that the main reactions that occurred in the alkali leaching and dilute acid washing were (3) and (8), respectively. The results were consistent with the XRD analysis. In addition, the elemental content changes in Tables 4 and 5 were also in accordance with the XRD analysis results. Therefore, the leaching mechanism of the process can be represented by Figure 13. It was observed that CaAl_2O_4 generated in alkali leaching, and it encapsulated the unreacted anorthite, causing the sodium hydroxide to not be able to further react with anorthite. This is the main reason for the low content of TiO_2 in the slag during the alkali leaching process. Thus, it is not an ideal way to deal with the low-grade Ti-slag by only using alkali leaching. However, CaAl_2O_4 can be removed by dilute acid washing. Therefore, the process of alkali leaching-dilute acid washing can avoid the encapsulation of the unreacted anorthite by the calcium aluminum spinel, which is the result of alkali leaching. If an acid leaching-alkali leaching process is employed to upgrade the low-grade titanium slag, silicic acid will be produced during the acid leaching process and encapsulate the unreacted anorthite. Although subsequent alkali leaching can remove the silicic acid, this process wastes a certain amount of the acid and alkali leaching agents. Thus, the alkali leaching-dilute acid washing process is more reasonable.

Figure 13. Schematic diagram of leaching mechanism.

4. Conclusions

(1) Thermodynamic analysis showed that the pH of alkali leaching should be higher than 13.50, whereas, that for dilute acid washing should be lower than 1.00. Increasing temperature was beneficial to alkali leaching, but it showed the opposite trend for dilute acid washing.

(2) The optimal alkali leaching conditions were NaOH concentration 2.8 mol/L (pH 14.44), L/S 4, temperature 95 °C, time 60 min. The optimal dilute acid washing conditions were HCl concentration

0.56 mol/L (pH 0.26), L/S 6, temperature 45 °C and time 60 min. Under the above optimum conditions, HQASTS was obtained with TiO₂ and Fe₂O₃ contents of 75.37 wt % and 0.96 wt %, respectively.

(3) Applying the HQASTS to the sulfate process can eliminate the processes of the freezing crystallization and separation of copperas, and it can realize the comprehensive utilization of titanium middling ore.

(4) The research of the leaching mechanism indicated that CaAl₂(SiO₄)₂ (anorthite) was transformed into CaAl₂O₄ (calcium aluminum spinel) after alkali leaching, and CaAl₂O₄ disappeared after dilute acid washing. The CaAl₂O₄ generated in alkali leaching would encapsulate the unreacted CaAl₂(SiO₄)₂, causing the NaOH to not be able to further react with CaAl₂(SiO₄)₂.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/9/8/460/s1>, Table S1: List of the preparation methods of synthetic rutile, Table S2: Verification experiments of predominant species (L/S 4), Figure S1: Effects of NaOH concentration on TiO₂ content at 55 °C and 95 °C, Figure S2: Effects of HCl concentration on TiO₂ content at 35 °C and 45 °C, Figure S3: Standard Gibbs free energy change of reactions.

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