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Improved Process for Separating TiO_2 from an Oxalic-Acid Hydrothermal Leachate of Vanadium Slag

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Abstract: In the present study, a process of separating high-quality TiO_2 from an oxalic-acid leachate of vanadium slag was proposed. It consists of two steps; oxalic acid was firstly recovered from the leachate by the cooling-crystallization method, and subsequently TiO_2 was separated from the oxalic-acid recovered leachate by the hydrothermal precipitation method. The experimental results indicate that oxalic acid can be recovered from the leachate by cooling crystallization at 5 °C, and after the recovery of oxalic acid, the purity of final TiO_2 product can also be improved. For example, when the leachate was cooled directly at 5 °C for 5 h, about 7% of oxalic acid was recovered, and the purity of final TiO_2 product improved from 95.7% to 96.6%. Furthermore, it was found that when some HCl solution was added to the leachate, both the recovery percentage of oxalic acid and the purity of TiO_2 product increased. For instance, when 15 vol% of HCl solution relative to pregnant leachate was added, about 35% oxalic acid was recovered by cooling crystallization at 5 °C for 3 h, and the anatase TiO_2 product with a purity of 99.2% was obtained by hydrothermal precipitation at 140 °C for 2.5 h.

Keywords: TiO_2; hydrothermal separation; oxalic-acid leachate; cooling crystallization

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1. Introduction

Vanadium titanomagnetite (VTM) ore is an important deposit, not only for its plenty reserves of vanadium, titanium, chromium, and iron but also for its globally abundant distribution in countries such as Russia, China, South Africa, New Zealand, Canada, and Australia [1,2]. In the VTM deposit, the principal oxide minerals are titanomagnetite ($Fe_{3-x}Ti_xO_4$) and ilmenite ($FeTiO_3$). In titanomagnetite, a small amount of vanadium and chromium exist simultaneously by substituting titanium [3]. After the beneficiation process of VTM, the obtained titanomagnetite concentrate is used as feedstock for iron-making, and ilmenite concentrate is used for producing titanium dioxide [4,5].

The titanomagnetite concentrate is generally smelted through the traditional blast furnace process, and liquid iron containing vanadium, titanium, and chromium is produced [4,6,7]. Then, to recover the vanadium that is reduced and dissolved in the liquid iron during the blast furnace smelting process, the liquid iron is blown in an oxygen-converter, which produces the vanadium, titanium, chromium, and some impurities, and some iron was oxidized to form a by-product called vanadium slag [8–10]. Although this by-product is generally called vanadium slag, a considerable amount of titanium and chromium is also contained in this it beside vanadium [11]. Typically, apart from 10~19% V_2O_3, 7~14% TiO_2 and 0.9~5% Cr_2O_3 exist in vanadium slag simultaneously. However, traditionally, vanadium slag was just adopted as a feedstock for vanadium production, and no more attention was paid to the recovery of titanium and chromium from vanadium slag.

Sodium salt roasting-water leaching and calcification roasting-acid leaching are the most common processes for vanadium production from vanadium slag [12–14]. In the sodium-salt-roasting–water-leaching process, the vanadium slag is roasted in an air atmosphere with the addition of sodium salt (one or a combination of NaCl, Na_2CO_3, or Na_2SO_4) to transform trivalent vanadium that occurs in vanadium slag in water-soluble sodium vanadate, and vanadium pentoxide is prepared by the following water-leaching, purification, precipitation, and calcination steps [12,15]. In the calcification roasting-acid leaching process, other than sodium salt, lime or limestone is used as an additive, and the trivalent vanadium that occurs in vanadium slag is transformed into acid-soluble calcium vanadate through roasting step and then leached by sulfuric acid [16,17]. No matter which of these two processes is adopted, only the vanadium that occurs in vanadium slag can be extracted. The valuable components of titanium and chromium that occur in vanadium slag are left in the residues, which causes not only an enormous waste of resources but also potential risk to the environment [18–20].

To solve the problems mentioned above, a novel approach to the co-extraction of vanadium, titanium, and chromium from vanadium slag was proposed in our previous publications [21,22]. The processes of co-extraction are as follows: firstly, the vanadium slag without roasting is directly hydrothermally leached by an oxalic-acid solution, by which the trivalent vanadium ion, tetravalent titanium ion, and trivalent chromium ion that occur in vanadium slag are simultaneously leached out; next, the separations of titanium oxide, vanadium oxide, and chromium oxide from the pregnant leachate are achieved through hydrothermal precipitation at temperatures higher than leaching. Based on this novel approach, the direct leaching coefficients of vanadium, titanium, and chromium in vanadium slag can reach 97.9%, 98.6%, and 93.3%, respectively, under the conditions of a temperature of 125 °C, an oxalic acid concentration of 25%, a liquid-to-solid mass ratio of 8:1, a reaction time of 90 min, the iron powder addition of 3.2%, and a stirring speed of 500 r/min. Additionally, a product of spherical anatase TiO_2 with a purity of 95.7% can be separated hydrothermally from the leachate after precipitation at 150 °C for 2.5 h [23].

This novel hydrothermal leaching and separation process is efficient and clean for the co-extraction of vanadium, titanium, and chromium from vanadium slag and for separating titanium oxide. However, two problems still need to be solved. One is that the consumption of oxalic acid needs to be reduced due to the relatively high price of oxalic acid. The other is that the quality or purity of the TiO_2 product need be improved. To these ends, in this study, a route of the cooling crystallization of oxalic acid from the leachate followed by the hydrothermal precipitation of TiO_2 was proposed and attempted. Unexpectedly, it was found that the cooling crystallization method was not only effective in recovering oxalic acid from the leachate but favorable for improving the purity of the TiO_2 product. So, after the effectiveness of the route was confirmed, the factors, such as acidity, temperature, etc., on the recovery extent of oxalic acid and quality of TiO_2 product were investigated systematically. Finally, an improved process of recovering oxalic acid and producing high-quality TiO_2 was presented.

2. Experimental

2.1. Co-Extraction of Vanadium, Titanium, and Chromium from Vanadium Slag

The detailed procedure for co-extraction can be found in previous publications [21,22]. For the sake of brevity, only the primary steps are narrated here. The used vanadium slag is analyzed by X-ray fluorescence spectroscopy (XRF-1800, Shimadzu Co., Ltd, Tokyo, Japan) and characterized by X-ray diffraction (XRD, MAC Science Co. Ltd., Kanagawa, Japan). The results indicated that it is composed of 10.61% V_2O_5, 8.65% TiO_2, 4.38% Cr_2O_3, 43.51% Fe_2O_3, 10.61% SiO_2, 7.98% MnO, 3.32% CaO, 3.08% MgO, and 1.64% Al_2O_3, and it is mainly constituted of spinel, olivine, and pyroxene mineral phases. About 1.25 g of vanadium slag, 0.04 g of iron powder, 10 g of distilled water, and 3.33 g of oxalic acid were placed into an autoclave of 50 mL; then, the leaching reaction was carried out at 125 °C for 90 min with a stirring rate of 500 r/min. After hydrothermal leaching reaction, the reacted mixture was

filtered and a pregnant leachate was obtained. This obtained pregnant leachate was used as the raw solution for recovery of oxalic acid and the separation of TiO_2. Its composition was determined by ICP optical emission spectrometer (ICP-OES, OPTIMA 7000DV, Waltham, MA, USA), and the results are presented in Table 1.

Table 1. Chemical composition of the pregnant leachate (g/L).

Elements	V	Ti	Cr	Fe	Mn	Si	Ca	Mg	Al
Concentration (g/L)	2.42	2.30	1.14	0.31	0.79	0.47	0.42	0.29	0.35

2.2. Recovery of Oxalic Acid from Leachate through Cooling Crystallization

About 20 mL of pregnant leachate was placed into a glass beaker; then, the beaker was placed into a thermoelectric cooling cup, which can hold the temperature constant at 5 °C. When the leachate was cooled for 20 min, about 0.02 g of oxalic acid was added as seed crystal. Thereafter, the leachate was stirred once every 10 min to make the temperature homogeneous.

In order to evaluate the recovery extent of oxalic acid, a tiny amount of leachate was taken out using a pipette during the cooling process at setting time intervals to track the change of oxalate concentration. The concentration of oxalate was measured by ion chromatography. Then, the percentage of recovery of oxalic acid was calculated according to Equation (1).

$$\beta = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

where β denotes the recovery fraction of oxalic acid, and C_t and C_0 signify the concentration of oxalate in leachate at the sampling time and the initial time, respectively.

2.3. Separation of TiO_2 from Oxalic-Acid Recovered Leachate

After a cooling crystallization reaction, the crystalized solid was filtered out. The filtered solid was identified by XRD, and its composition was measured by ICP-OES. The obtained filtrate, which is referred to as oxalic-acid recovered leachate in the following text, was further used for the separation of TiO_2.

About 15 mL of oxalic-acid recovered leachate was placed into a 50 mL autoclave to perform the hydrothermal precipitation reaction for 2.5 h. Additionally, the hydrothermal temperature, as well as the property of the oxalic-acid recovered leachate, were changed to investigate their effects on the precipitation extent and purity of TiO_2.

After precipitation reaction, the precipitate was filtered out. Then, XRD measurement was performed to identify its phase structure, ICP-OES measurements were carried out to determine the impurity and the purity of the product, and SEM measurements were adopted to characterize the morphology of the product.

To determine the hydrothermal precipitation fraction of titanium from the oxalic-acid recovered leachate, the concentration of titanium in oxalic-acid recovered leachate, $C_{Ti,i}$, and the concentration of titanium in the filtrate after hydrothermal precipitation reaction, $C_{Ti,f}$, were measured by ICP-OES. Then, the precipitation fraction of titanium, η, was calculated according to Equation (2).

$$\eta = \left(1 - \frac{C_{Ti,f}}{C_{Ti,i}}\right) \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Practicability of the Design for Recovery of Oxalic Acid and Separation of TiO_2

The design of this study consists of two steps; one is to recover oxalic acid from the pregnant leachate through the cooling crystallization method, the following is to separate TiO_2 from the oxalic-acid recovered leachate by the hydrothermal precipitation method. So, first of all, the feasibility of the whole design was confirmed.

To perform the confirmation, the pregnant leachate with a composition shown in Table 1 was directly cooled to 5 °C and held for 5 h; then, the crystalized precipitate was filtered out and identified by XRD measurement. The measured XRD pattern is shown in Figure 1, from which it can be seen that the obtained precipitate is the well crystalized oxalic acid phase.

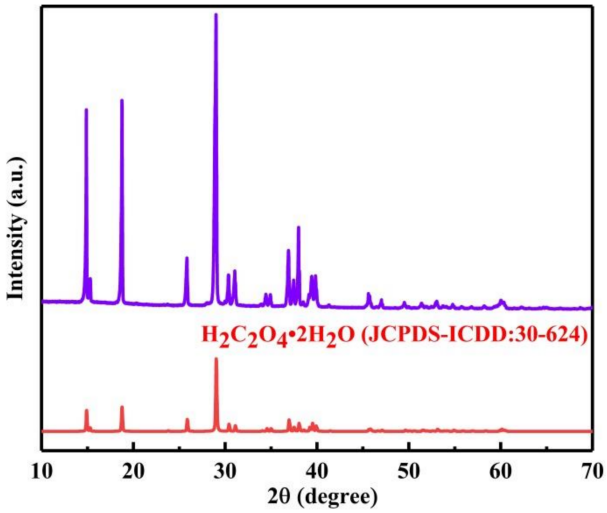


Figure 1. XRD pattern of the precipitate by cooling crystallization.

To further estimate the purity of the obtained oxalic acid phase, it was analyzed by ICP-OES. The contents of the main impurities are shown in Table 2. From the contents of impurities, the purity of the crystalized oxalic acid can be estimated to be higher than 99%.

Table 2. Contents of main impurities in the crystalized oxalic acid phase.

Elements	Fe	Ca	Si	Others
Content (wt. %)	0.03	0.02	0.06	trace

In the following step, the oxalic-acid recovered leachate was directly used for separating TiO_2 by hydrothermal precipitation method. The sample was heated to 140 °C in autoclave and held for 2.5 h; then, the sample was filtered. The solid phase filtered out was identified by XRD, and its composition was determined by ICP-OES.

Figure 2 shows the measured XRD pattern. By comparison with the standard pattern of anatase TiO_2 shown together in Figure 2, it can be seen that the obtained solid product is single-phase TiO_2 with an anatase structure. The composition of the product measured by ICP-OES is shown in Table 3, which indicates that the purity of the product is acceptable.

To evaluate the effect of recovering oxalic acid on the quality of the obtained TiO_2 product, our previous reported results were adopted as a reference for comparison. In our previous study [23], the pregnant leachate without the recovery of oxalic acid was used as a raw material of hydrothermal precipitation. The composition of the obtained TiO_2 product, as shown in Table 4, is cited.

By comparing the composition in Table 3 with that in Table 4, it can be seen that the purity of TiO_2 is improved slightly. Especially, the contents of V_2O_5 and Cr_2O_3 impurities can be reduced through recovering oxalic acid from the pregnant leachate.

The above results indicate that not only is the design of the present study feasible, it is also favorable for improving quality of the TiO_2 product.

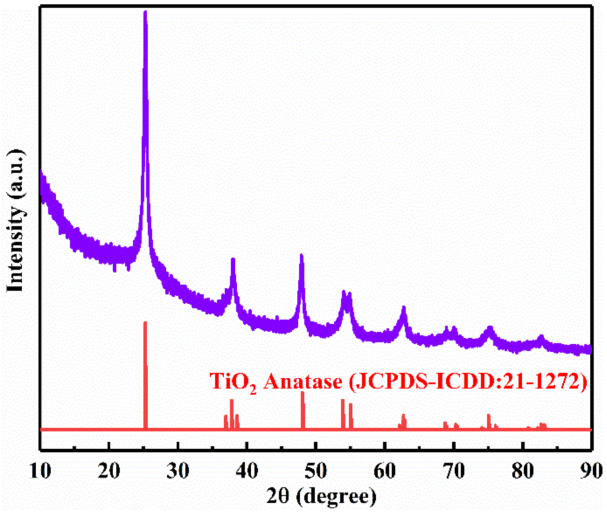


Figure 2. XRD pattern of the precipitate by hydrothermal precipitation.

Table 3. Composition of the product of hydrothermal precipitation.

Components	TiO_2	V_2O_5	Cr_2O_3	Fe_2O_3	MnO	SiO_2	CaO	MgO	Al_2O_3
Content (wt. %)	96.6	1.08	0.01	0.29	0.22	1.19	0.24	0.05	0.26

The content of TiO_2 was obtained by subtracting the contents of impurities.

Table 4. Composition of the TiO_2 product in previous study [23].

Components	TiO_2	V_2O_5	Cr_2O_3	Fe_2O_3	MnO	SiO_2	CaO	MgO	Al_2O_3
Content (wt. %)	95.7	2.44	0.10	0.24	0.15	1.27	0.04	0.03	<0.01

The content of TiO_2 was obtained by subtracting the contents of impurities.

3.2. Optimization of the Oxalic-Acid Recovering Process

Now that oxalic acid can be recovered from the pregnant leachate by the cooling crystallization method, the more effective conditions for recovering oxalic acid need to be further investigated. We know that oxalic acid is a weak acid; four species (H^+, $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$) exist in its aqueous solution. Inspecting the chemical reactions among these species, it can be concluded easily that increasing the concentration of H^+ will definitely cause an increase in $H_2C_2O_4$ content. The effect was calculated according to their chemical equilibrium reactions, and the results are shown graphically in Figure 3.

From Figure 3, it can be seen clearly that the content of the $H_2C_2O_4$ molecule increases significantly when the pH value is less than 2. This increase in content for the $H_2C_2O_4$ molecule will promote its crystallization and precipitation. Hence, by adding HCl solution into pregnant leachate to change its pH value, the effect of acidity on the percentage of recovery of oxalic acid was studied.

A HCl solution with a concentration of 36.64% was used as the additive, and three different adding amounts 5 vol%, 10 vol%, and 15 vol% relative to the pregnant leachate were investigated for comparison. After adding HCl solution, the pregnant leachate was placed into a cooling cup of 5 °C. At various time intervals, sampling was carried out to monitor the change of oxalate concentration in pregnant leachate, and the percentage of recovery of oxalic acid by cooling crystallization was calculated. The obtained results at various conditions are exhibited in Figure 4.

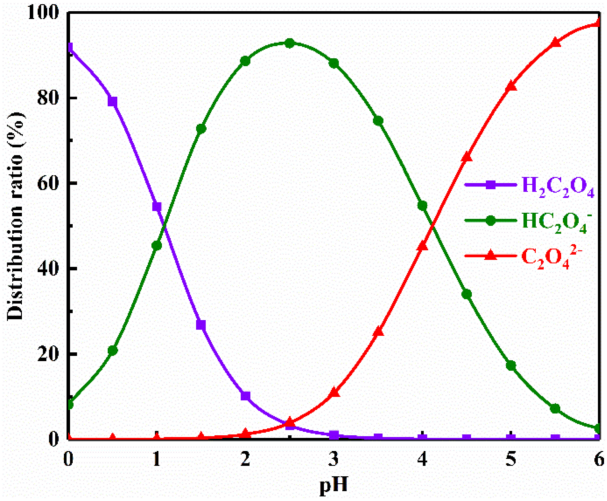


Figure 3. Effect of pH value on the distribution of various species in oxalic acid solution.

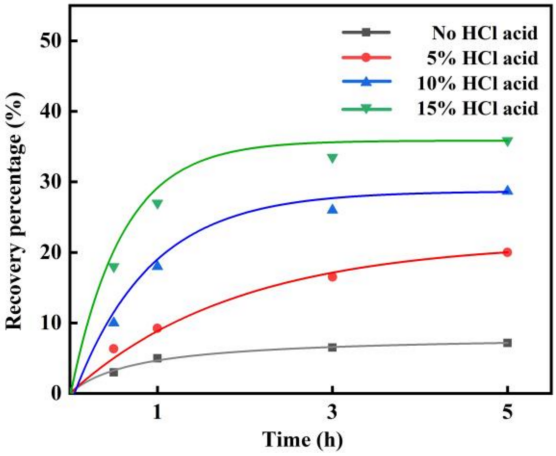


Figure 4. Recovery extent of oxalic acid at various HCl adding conditions.

From the results shown in Figure 4, it can be found that, compared with the case without adding HCl, both the extent and the rate of recovery of oxalic acid increased sharply. When 15 vol% HCl was added, the percentage of recovery reached about 35% after cooling crystallization for 5 h, which is about seven times higher than no adding of HCl and about two times higher than the case of adding 5 vol% HCl. Concerning the rate of recovery, the recovery fraction reached nearly to the maximum after 1 h when 15 vol% HCl was added, whereas 3 h was need to reach the maximum when 10 vol% HCl was added. Hence, from the perspective of recovering oxalic acid, adding 15 vol% is favorable for improving the recovery efficiency.

3.3. Optimization of the TiO_2 Separating Process

By adding HCl solution, the recovery fraction of oxalic acid can be improved significantly. Then, the effect of the added HCl on the following step, i.e., the hydrothermal precipitation of TiO_2, needs to be evaluated. So, the effects on hydrothermal temperature, precipitation extent, and the quality of produced TiO_2 were investigated.

About 15 mL leachate of oxalic acid recovered was placed into a 50 mL autoclave and then heated and held at different temperatures of 120 °C, 130 °C, 140 °C, and 150 °C, respectively, for 2.5 h. After hydrothermal precipitation, the filtered solid was identified by XRD and analyzed by ICP-OES to determine the contents of impurities, while the filtrate was also analyzed by ICP-OES to measure the content of Ti to determine the precipitation extent.

In Figure 5, the effects of the added amount of HCl solution, as well as the hydrothermal temperature, on the precipitation fractions of TiO_2 are presented. By comparing the results shown in Figure 5 with the case of no HCl added, it can be found that by adding HCl, the precipitating temperature can be lowered significantly. For example, without adding HCl, almost no TiO_2 was precipitated at 120 °C, whereas when 5 vol% HCl solution was added, the precipitation fraction of TiO_2 was already higher than 90% at 120 °C, reaching 96.5% at 130 °C, and was close to the complete extent at 140 °C. However, with the further addition of HCl, this positive effect on the precipitating temperature will deteriorate firstly and then resume gradually. As 10 vol% HCl solution was added, the precipitation fractions of TiO_2 at all temperatures were less than the 5 vol% HCl solution added case; then, when 15 vol% HCl solution was added, the degraded precipitation fraction showed a recovering trend. This change of precipitation extent of TiO_2 implies that the adding of HCl causes the change of occurrence state of species in solution, which needs to be elucidated deeply in the future work.

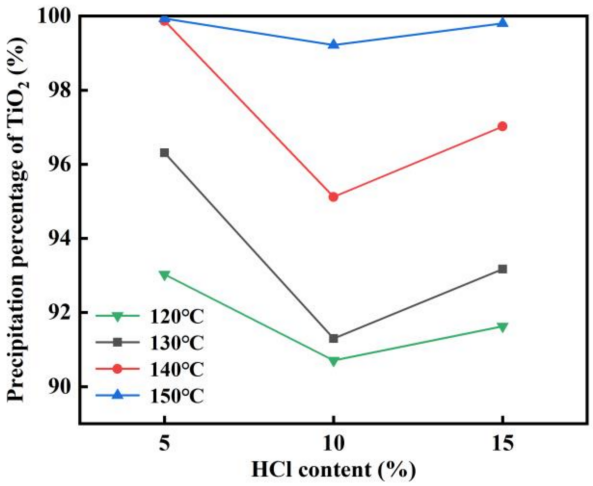


Figure 5. Effects of added HCl on the hydrothermal precipitation extent of TiO_2.

Since the hydrothermal precipitation extent at 140 °C for each case is relatively high and acceptable, the precipitates obtained at this temperature were used to characterize the quality of the product. Firstly, their phase structures were identified by XRD; the measured patterns are shown in Figure 6. It can be seen that the adding of HCl has almost no effect on the structure and crystallinity of the product. Although the crystallinity of the products is not perfect, they can be easily identified as anatase TiO_2 through comparison with standard pattern.

The contents of impurities in the products measured by ICP-OES are summarized in Table 5, where the contents for TiO_2 were calculated by subtracting all impurities. As can be seen, the purity of the product increases gradually when more HCl is added. When 15 vol% HCl solution was added, a product with TiO_2 content higher than 99% was obtained.

To provide an overview of the effect of added HCl on the contents of impurities, their changing trend with an increasing amount of added HCl is summarized in Figure 7. It can be seen that, apart from MgO and Cr_2O_3, the content of the other impurities can be suppressed to some extent through adding HCl. Especially, the impurities V_2O_5, Al_2O_3, and MnO can be eliminated effectively.

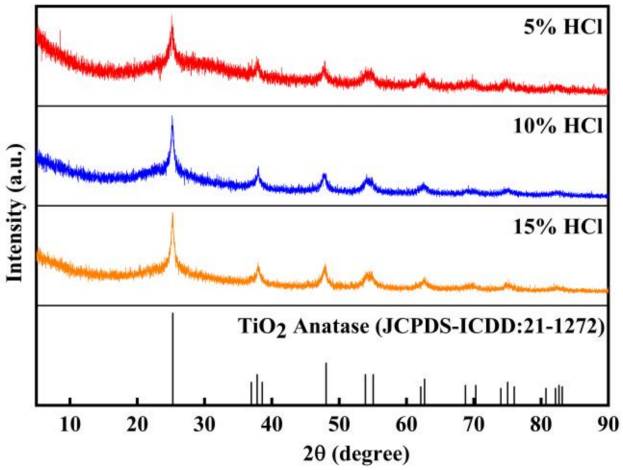


Figure 6. XRD patterns of the hydrothermal product obtained at 140 °C.

Table 5. Compositions of hydrothermal precipitation product at 140 °C (wt. %).

Sample	TiO_2	V_2O_5	Cr_2O_3	Fe_2O_3	MnO	SiO_2	CaO	MgO	Al_2O_3
No HCl added	96.6	1.08	0.01	0.29	0.22	1.19	0.24	0.05	0.26
5 vol% HCl added	96.4	0.09	0.06	0.1	0.04	2.81	0.29	0.03	0.11
10 vol% HCl added	98.1	0.08	0.03	0.1	0.02	1.37	0.15	0.03	0.04
15 vol% HCl added	99.2	0.07	0.03	0.1	0.01	0.36	0.11	0.04	0.03

The content of TiO_2 was obtained by subtracting the contents of impurities.

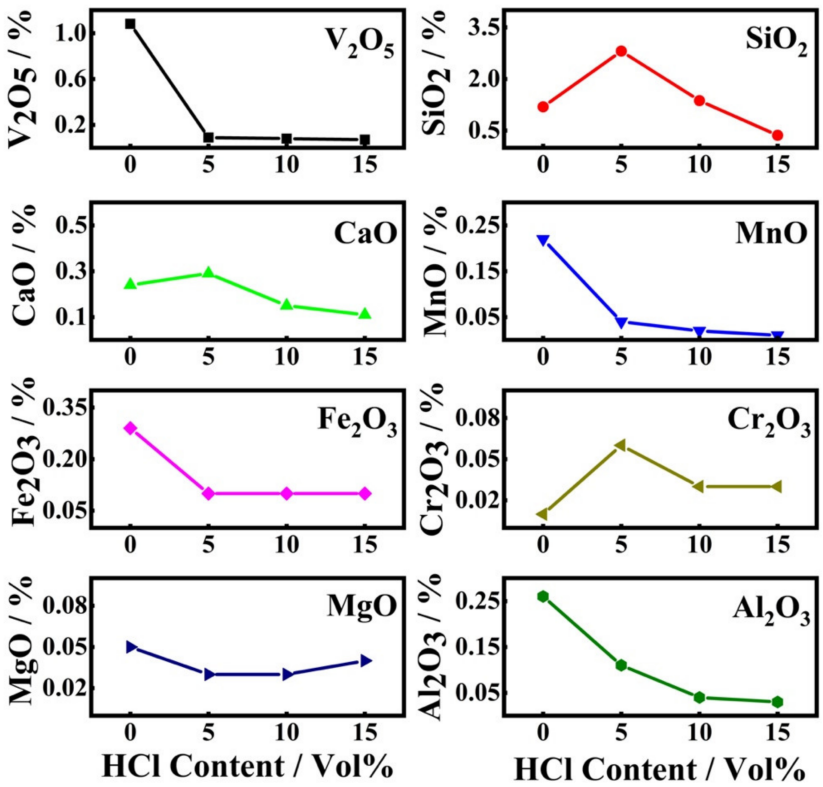


Figure 7. Effect of added HCl on the changing trend of impurities in TiO_2 product.

To further inspect the effect of added HCl on the micromorphology of hydrothermal product, the products of various HCl adding amounts were observed through SEM, and the typical micrographics of the products are shown in Figure 8. It can be seen that

both the particle size and the morphology of the product were altered significantly after HCl was added to the pregnant leachate. The possible reason may be adding HCl can promote the recovery of oxalic acid and subsequently cause a remarkable decrease in oxalate concentration in solution. With the decrease in the oxalate concentration, the decomposing temperature for the complex of Ti ions and oxalate may be lowered, which will ultimately influence the hydrothermal precipitating extent as well as the morphology of the product.

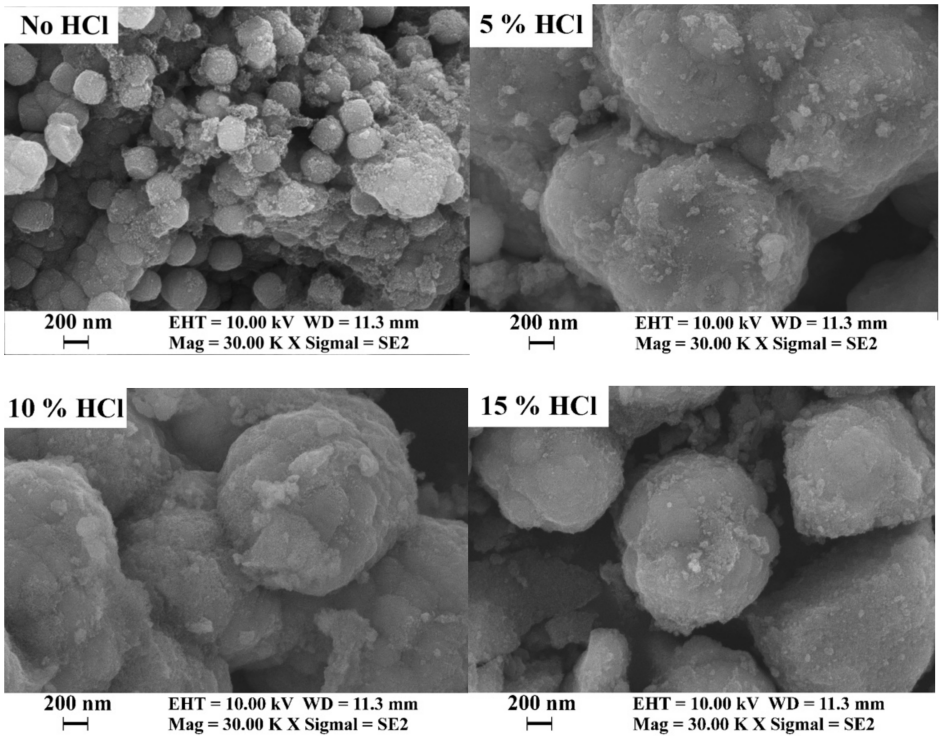


Figure 8. Effect of added HCl on the changing trend of impurities in TiO_2 product.

4. Conclusions

As one of a series of studies about the clean and efficient utilization of vanadium slag, this study is concerned with the processing of a Ti-bearing oxalic acid hydrothermal leachate of vanadium slag. From an economic point of view, a process of first recovering part of the oxalic acid from the pregnant leachate by the cooling crystallization method and then separating TiO_2 by the hydrothermal precipitation method was designed. The experimental results confirmed that this process is not only feasible but also favorable for improving the quality of the separated TiO_2 product. Then, an optimization of the process was carried out, and the obtained results are as follows:

(1) Adding some HCl to the pregnant leachate can further improve the recovery extent and rate of oxalic acid. When 15 vol% HCl was added, the recovery percent of oxalic acid reached about 35% after cooling crystallization at 5 °C for 3 h, which is about seven times higher than the recovery percent when not adding HCl and about two times higher than the recovery percent when adding 5 vol% HCl.

(2) The adding of HCl in the pregnant leachate does not result in negative effects on the hydrothermal precipitation of TiO_2 from the leachate. Additionally, it helps to ameliorate the quality of the precipitated TiO_2. When 15 vol% HCl was added, the TiO_2 product with a purity higher than 99.2% was obtained.

Author Contributions: Conceptualization Q.M. and M.L.; methodology, G.G.; formal analysis, W.Z.; draft preparation J.Z.; funding acquisition, project administration, B.Y. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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