Kinetics of sulphuric acid leaching of titanium from refractory anatase under atmospheric pressure

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Abstract: Anatase, as an important titanium resource, is attracting more and more attention in research and application. In this study, an efficient process of comprehensively extracting the titanium and other valuable elements from the anatase mineral was proposed. The effect of particle size, stirring speed, initial sulphuric acid concentration, solid-to-liquid ratio, and reaction temperature on the leaching rate of titanium from anatase was investigated. Under appropriate two-stage countercurrent leaching conditions, with the first stage of the liquid-to-solid ratio of $1/3$ g/cm³, reaction temperature of 120 °C, initial acid concentration of 11 mol/dm³, residence time of 30 min, stirring speed of 200 rpm, and the second stage of the liquid-to-solid ratio of $1/3$ g/cm³, reaction temperature of 200 °C, initial acid concentration of 13 mol/dm³, residence time of 30 min, and stirring speed of 200 rpm, over 99% TiO_2, 99% Al_2O_3, and 97% Sc_2O_3 were extracted respectively with quartz still remained in the residue. X-ray diffraction, X-ray fluorescence spectrometer, and scanning electron microscopy/energy-dispersive spectroscopy were used to characterize the anatase samples before and after the leaching. Additionally, the leaching kinetics analysis indicated that both acid concentration and temperature were the most significant parameters for the leaching process. And, the titanium leaching reaction rate was controlled by the diffusion of reactants through the residual layer.

Keywords: anatase ore, kinetics, sulphuric acid, leaching, titanium dioxide

1. Introduction

Anatase, as a Ti-bearing independent mineral with industrial value, is less common than rutile and ilmenite in the world. However, with the continuous consumption of the titanium resource, anatase has been appreciated and utilized (Whitehead., 1983; Rhee and Sohn., 1990). A large deposit of anatase occurs as residual-deluvial-type deposit in the southwestern area of China has been discovered recently (Zhang et al., 2014 a). The scale of the anatase deposit has been deeply surveyed; the result shows that it contains approximately 23.06 million tons of anatase, which is found at an average concentration of 4.39%. The potentially valuable exploitable minerals associated with the anatase are kaolinite, sericite, and quartz, which coexist with each other closely, and presenting in fine grain size (Zhang et al., 2014 a; Zhang et al., 2014 b). The anatase deposit is difficult for dressing and smelting, and not currently being exploited but there is being great commercial interest in developing it.

Although titanium is the ninth most abundant element in the earth's crust, it is considered to be a rare metal as it is highly dispersed and very difficult to extract (Temple., 1996; Nayl et al., 2009; Das et al., 2013). With the development of technologies, titanium has been extensively used in alloys, paints, paper, porcelain, and plastics (Samal et al., 2008; Han et al., 2012). The demand for titanium for use as pigment and alloys has been growing nowadays. The global production capacity of titanium dioxide pigment increased to 6.5 million tons in 2012 (U.S. GeologicalSurvey., 2013). The output of titanium metal sponge has also increased steadily to 214000 tons in 2012, equivalent to 4.2 times of the output in 1997 (U.S. GeologicalSurvey., 2013), and the demand for titanium was expected to continue to grow for a long time in the future (Zhang et al., 2011).

Rutile and ilmenite are the main commercial ores of titanium, while anatase has been paid great attention as the most important potential resource (Barksdale., 1950; Whitehead., 1983; Rhee and Sohn., 1990). With the gradual exhaustion of rutile, efforts have been devoted into extracting titanium from other still abundant resources, including ilmenite and anatase (Sarker et al., 2006; Gambogi., 2009). Nevertheless, most of the studies are focused on the extraction of titanium from ilmenite, there has been very few published essays on extraction of titanium from anatase minerals (Liu et al., 2013; Sui and Zhai., 2014; Liu et al., 2014). The sulphuric acid leaching process is the most effect way for processing low grade titanium resources (Kolen'Ko et al., 2003; Akhgar et al., 2010; Zhang et al., 2011). Conventional titanium mineral processing involves sulphuric acid leaching at 130~170℃ (Welham and Llewellyn, 1998; Sasikumar et al., 2007; Kalinkin and Kalinkina., 2011). However, there are some drawbacks in the conventional direct sulphuric acid leaching route, such as silica gel formation, low selectivity towards valuable metals, low recovery rate, etc (Kalinkin and Kalinkina., 2011). Some novel leaching processes, aiming more efficient and selective leaching but also considering environmental aspects via lower acid consumption, have been investigated recently. Alkan et al. (2018) reported that silica gel was not formed, and high titanium leaching efficiency was achieved when hydrogen peroxide was introduced into the system of sulphuric acid leaching titanium from bauxite residue. Kalinkin and Kalinkina. (2011) investigated sulphuric acid leaching of mechanically activated titanite. It was found that after preliminary mechanical activation in the laboratory centrifugal-planetary mill, the leaching rate of titanite concentrate was remarkably increased, an about 90% Ti in titanite was solubilized after dry mechanical activation whereas similar leaching of unactivated titanite yielded about 1% Ti dissolution only. Ultrasonic wave was also introduced to promote the leaching efficiency of titanium in the sulphuric acid, and it was considered as an efficient method. Ultrasound power is a major parameter influencing titanium recovery efficiency (Lim and Shon., 2008). Agatzini-Leonardou et al. (2008) reported a laboratory-scale research on the leaching anatase in red mud with diluted sulphuric acid. It was found that temperature and acid normality have a considerable effect on the leaching efficiency of the titanium. The recovery efficiency of titanium is low under the diluted sulphuric acid condition.

In the present study, the comprehensive recovery of ion, titanium, scandium, aluminum, and silicon from the anatase by sulphuric acid leaching was studied. The optimal process conditions for the sufficient utilization of the anatase, and the leaching kinetics of titania dissolution were investigated carefully. The effects of particle size, agitation speed, initial sulphuric acid concentration, solid-to-liquid ratio, and reaction temperature on the leaching efficiency of the anatase were studied. The flowsheet of the sulphuric leach stage was eventually proposed.

2. Materials and methods

2.1. Materials

The anatase sample used in this study was a residual-deluvial-type mineral obtained from a deposit in southwestern China (Zhang et al., 2014 a; Zhang et al., 2014 b). Most of the titanium occurs as micro-fine-grained anatase embraced in altered basalt, and associated with feldspar, limonite, kaolinite, and quartz closely. The disseminated grain size of the sample was below 5 μm. Preliminary laboratory ore-dressing experiments indicated that the anatase mineral was difficult to process. The composition of the anatase was analyzed by X-ray fluorescence spectrometer (XRF, ZSX100e, Rigaku, Japan), and the results are presented in Table 1, it is worth noting that it contains a lot of scandium.

Table 1. Chemical analysis of the anatase

Element	Sc_2O_3(ppm)	TiO_2	TFe	As(ppm)	Al_2O_3	P	CaO
Wt%	84.7	5.30	16.85	22.3	22.18	0.10	0.064
Element	K_2O	SiO_2	Na_2O	Total RE	MgO	S	/
Wt%	1.04	35.75	<0.1	0.04	0.76	0.02	/

The mineralogical phases of the anatase were investigated by XRD (XRD, D/Max 2200, Rigaku, Japan) and scanning electron microscope (SEM, XL30ESEM-TM, Philips, Holland) equipped with energy disperse X-ray spectrometer (EDS, EDAX Genesis, USA). The XRD pattern of the anatase is

shown in Fig. 1. The results of mineralogical analysis showed that the samples contained about 5.3% w/w anatase, 48% kaolinite, 25% limonite, 9% sericite, 9% quartz, and other minor minerals. The analytically pure sulphuric acid used in the experiments was obtained from Chengdu Chemical Co., Ltd. Sichuan. All of the chemical reagents used in this study were of analytical grade.
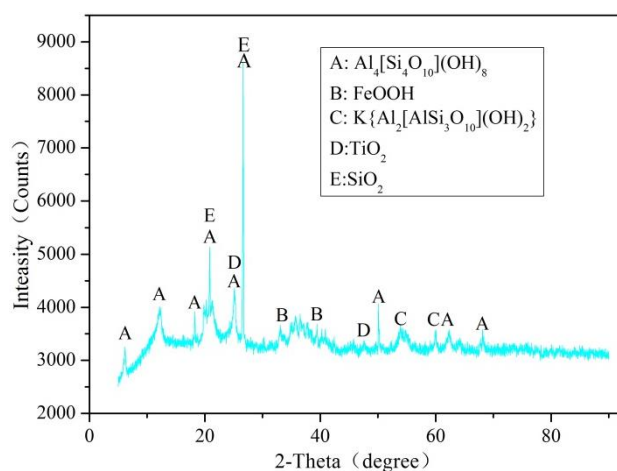

Fig. 1. XRD patterns of the anatase sample

2.2. Methods

The batch leaching experiments were conducted in self-made devices, which contained a 1 dm^3 cylindrical glass reactor, a reflux condenser, a heating element, a mechanical stirring, and a bath thermometer. A volume of 500 cm^3 H$_2$SO$_4$ solution was added to the reactor firstly. After the temperature of the solution reached the desired value, the stirrer was started, and the sample was added to the reactor. The evaporated leaching solution returned to the reaction system from the reflux condenser. A 1 cm^3 sample of slurry was withdrawn at the desired time interval, and filtered quickly while it was still hot, and the leachate was determined by inductively coupled plasma spectrometer (ICPS-1000Ⅱ, Shimadu, Japan).

The leaching rate of the titanium dioxide was calculated using Eq. (1):

$$X = \frac{V \times b}{M_1 \times c} \tag{1}$$

where M_1 is the mass of the anatase ore samples used in the batch experiment, g; c is the content of titanium dioxide in the raw ore, wt. %; V is the volume of the leachate, cm^3; b is the titanium dioxide concentration of the leachate, g/ cm^3.

3. Results and discussion

3.1. Effect of particle size

In general, the decrease in the particle size of sample enhances the metal dissolution. The effect of feed size was studied under the conditions of reaction temperature of 100 ℃, H$_2$SO$_4$ concentration of 5 mol/dm^3, solid-to-liquid ratio of 1:3 g/cm^3, stirring speed of 200 rpm, and retention time of 60 min. The results are seen in Fig. 2. as expected the titanium leaching rate increased with the decreasing particle size. The increasing rate was sharp in the fraction of -74 μm was less than 75% range, and became mild in the fraction of -74 μm was more than 75% range. The leaching rate of titanium increased with the decrease of particle size because the decrease of particle size increased both the specific surface of the titanium slag and its reactivity, and as the particle size decreased further, this effect gradually decreased. In the subsequent experiments particle size of the fraction of -74 μm 75% was used.
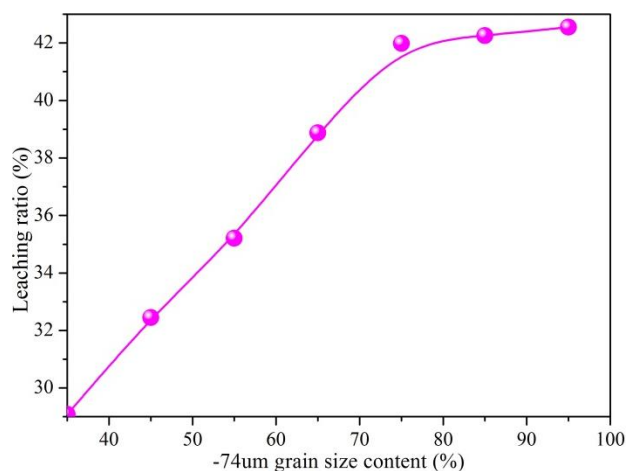
Fig. 2. Effect of -74 µm content of the feed on the extractions of TiO$_2$

3.2. Effect of stirring speed

To allow efficient reaction in the acid leaching processes, the stirring speed is required to suspend the particles. The effect of agitation on the leaching process was investigated using 5 mol/dm^3 H$_2$SO$_4$ solution with the solid-to-liquid ratio of 1:3 g/cm^3 at temperature 100 ℃, and stirring speed ranging from 100 rpm to 500 rpm. The results of TiO$_2$ leaching from the anatase at different agitation speeds are shown in Fig. 3, which showed that agitation speed had a little effect on the anatase dissolution in the range of 200~500 rpm. In this case, solid particles remain suspended in solution homogeneously. The agitation speed of 200 rpm was kept in the subsequent tests.
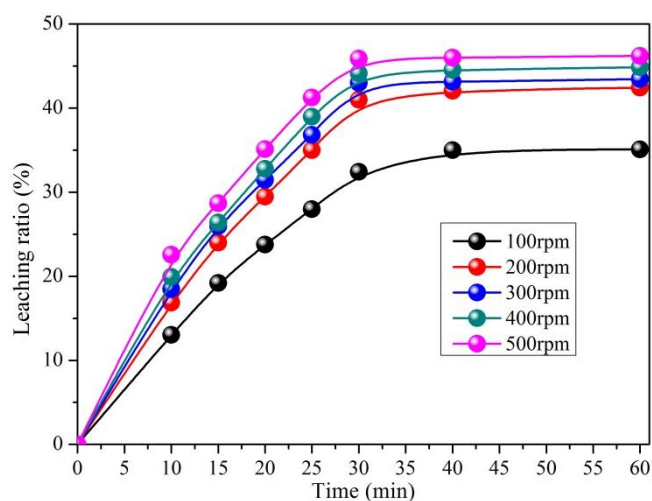

Fig. 3. Effect of stirring speed on the extractions of TiO$_2$

3.3. Effect of initial H$_2$SO$_4$ concentration

The experiments for the effect of H$_2$SO$_4$ concentration were carried out with the H$_2$SO$_4$ concentrations varying from 3 mol/dm^3 to 13 mol/dm^3 under other parameters of stirring speed of 200 rpm, temperature of 100 ℃, solid-to-liquid ratio of 1:3 g/cm^3. The result is seen in Fig. 4, the leaching rate of the TiO$_2$ increased significantly with the acid concentration increase from 3 mol/dm^3 to 12 mol/dm^3, after which there was a small increase with the further increase to 13 mol/dm^3. Of all the valuable metal elements in this ore, titanium is the most difficult to be leached. High sulphuric acid concentration should be selected for the efficient leaching of valuable metals in the ore. However, the elements of Sc, Ti, Al, Fe are known as low solubility in high sulphuric acid concentrations at room temperature because of the formation of surface dense oxide films (Li., et al., 2007; Xiong., et al., 2013). The heating leaching process is an effective technique in metal hydrometallurgical field, which can promote the leach reaction

kinetics of leaching reaction and obtain higher metal recovery by treating refractory ore (Welham and Llewellyn, 1998; Sasikumar et al., 2007; Kalinkin and Kalinkina., 2011). The experimental results showed that high metal leaching rate was obtained by applying concentrated sulphuric acid under heating condition. The sulphuric acid concentration of 11 mol/dm^3 was kept in the subsequent tests.
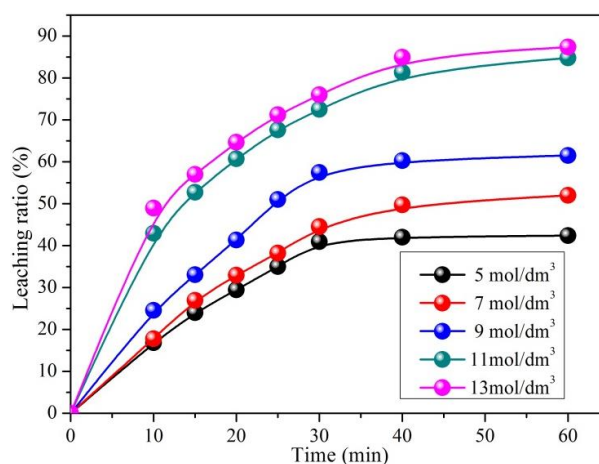

Fig. 4. Effect of initial sulphuric concentration on the extractions of TiO_2

3.4. Effect of temperature

Early exploration experiments show that heating is necessary for the efficient leaching of titanium from anatase. More importantly, silica gel is formed in the leachate at a lower temperature, resulting in the inability of solids and liquids to separate. Therefore, temperature is an important parameter in the leaching process.
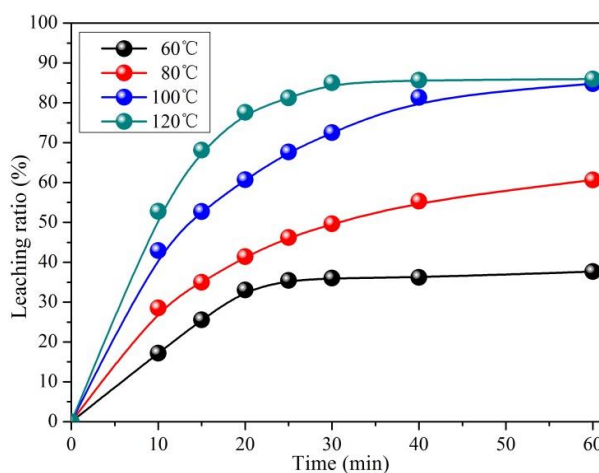

Fig. 5. Effect of temperature on the extractions of TiO_2

As the sulphuric acid concentration rises, the boiling point of the leach liquor increases. The boiling point of the 11 mol/dm^3 of sulphuric acid leachate is as high as about 170 ℃. The effect of temperature on the TiO_2 leaching efficiency was examined with temperature ranging from 60 ℃ to 120 ℃, under stirring speed of 200 rpm, sulphuric acid concentration of 11 mol/dm^3, solid-to-liquid ratio of 1:3 g/cm^3. From the result depicted in Fig. 5, we can see that with the increase of temperature, the TiO_2 leaching efficiency increased significantly. At 60 ℃, only 36.01% TiO_2 was leached then increased to 85.04% at 120 ℃ in 30 min. The temperature of 120 ℃ was kept in the subsequent tests.

3.5. Effect of solid-to-liquid ratio

The influence of solid-to-liquid ratio on the TiO_2 leaching extent was investigated with the other parameters were fixed at sulphuric acid concentration of 11 mol/dm^3, leaching temperature of 120 ℃,

stirring speed of 200 rpm. The result is seen in Fig. 6. The leaching ratio was affected remarkably in high solid-to-liquid ratio range, and became mild in citric acid addition ratio range. The TiO_2 leaching ratio increased from 65.93 % at the solid/liquid ratio of 1:2 g/cm^3 to 85.04% at the solid-to-liquid ratio of 1:3 g/cm^3 in 30 min. As the solid-to-liquid ratio drops to lower than 1:3 g/cm^3, TiO_2 leaching efficiency increased slowly. Therefore, solid-to-liquid ratio of 1:3 g/cm^3 was considered to be the optimum value. It is worth noting that the leaching reaction was almost completed within 30 minutes.
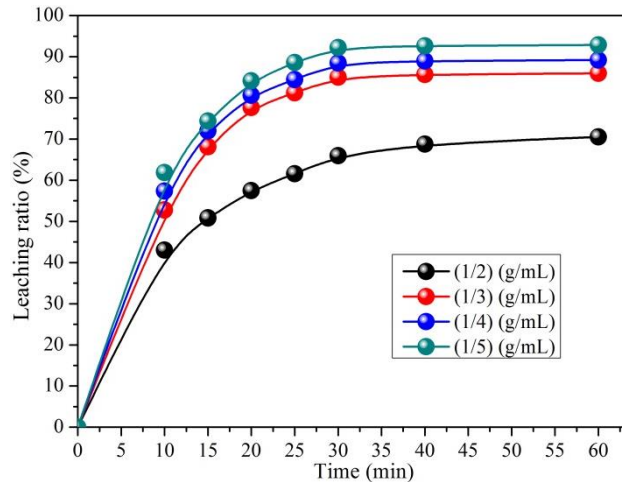

Fig. 6. Effect of solid-to-liquid ratio on the extractions of TiO_2

3.6. The change of morphology of anatase

The morphology and the surface elemental composition of anatase particles before and after the leaching were examined by SEM-EDS, and the results in Fig. 7 showed that the anatase mineral is high-density, after sulphuric acid leaching the morphology of titanium slag was destroyed; the solid leaching residues present a rough and porous surface. During the leaching process, the anatase mineral was not completely dissolved, but left a portion of the residue that was insoluble in sulphuric acid. According to the EDS analysis results, seen in Fig. 8, the main element of the surface of the residue was Si, while Ti content reduced greatly, which proved the existence of a solid product layer.

3.7. Kinetic analysis

There are the unreacted residue existed after the sulphuric acid leaching process, so the experimental results were analyzed by the shrinking-core model (Velardo et al., 2002). Assuming the anatase particles is homogeneous and spherical. If the leaching rate is governed by the chemical reaction, the acid leaching kinetics of the process can be described using the following equation of the shrinking-core model:

$$1 - (1 - X)^{1/3} = k_r \cdot t \tag{2}$$

However, if the leaching rate is governed by the internal diffusion, the acid leaching kinetics of the process can be described using the following equation of the shrinking-core model:

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = k_d \cdot t \tag{3}$$

where X is the acid leaching rate of titanium dioxide, t is the leaching time, k_r is the rate constant of leaching reaction, k_d is the rate constant of internal diffusion (Levenspiel., 1972).

The apparent activation energy of anatase extraction can be analyzed by the following Arrhenius equation:

$$\ln K = \ln A - \frac{E_a}{RT} \tag{4}$$

where k is the apparent rate constant, E_a is the apparent activation energy, A is the frequency factor, R is the universal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$), and T is the reaction temperature in K.
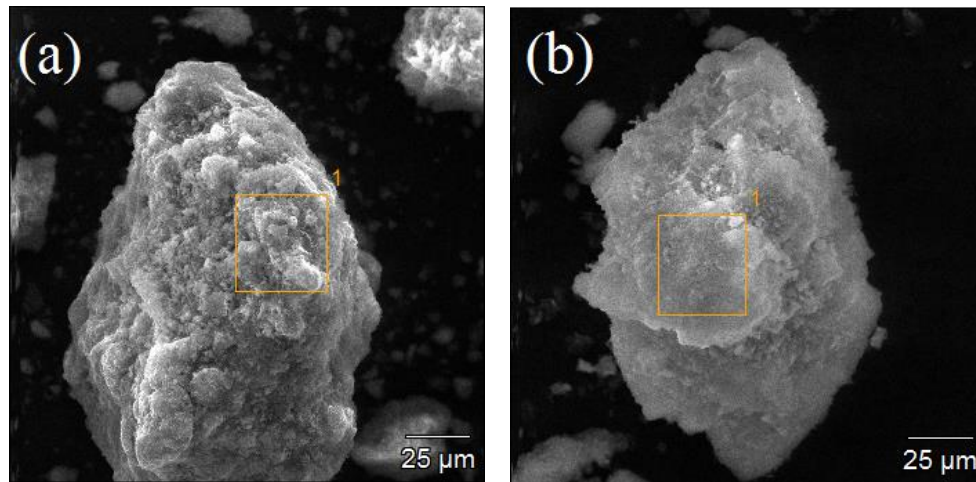
Fig. 7. Morphology of the anatase samples, (a) before leaching, (b) after leaching (11 mol/dm³ H₂SO₄, stirring speed 200 rpm, S/L 1/3 g/cm³, temperature 120 °C, time 30 min)
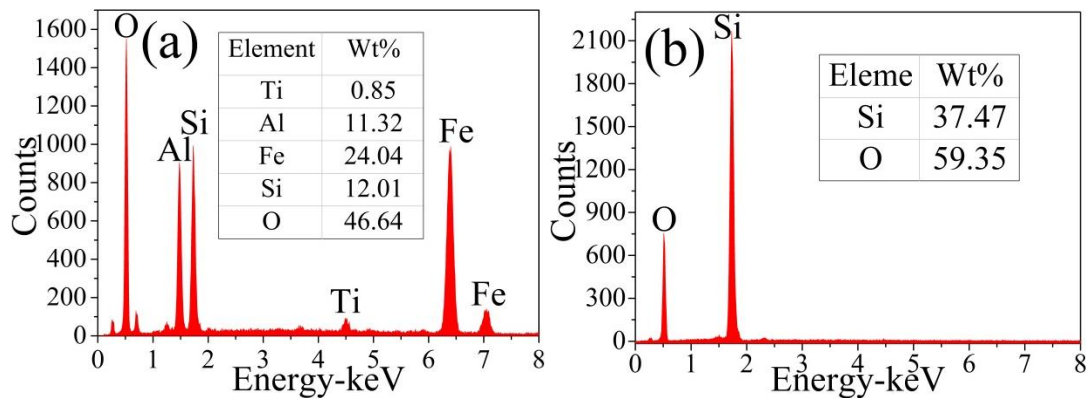

Fig. 8. EDS patterns of the anatase samples, (a) before the leaching, (b) after the leaching (11 mol/dm³ H₂SO₄, stirring speed 200 rpm, S/L 1/3 g/cm³, temperature 120 °C, time 30 min)

The data presented in Fig. 4, are plotted according to Eq. (2) and Eq. (3) respectively, the results are shown in Fig. 9 (a) and (b). The results indicate that the anatase leaching process is governed by the chemical reaction in the low sulphuric acid concentration arrangement of 5 mol/dm³~9 mol/dm³, and in the high sulphuric acid concentration arrangement of 9 mol/dm³~13 mol/dm³, the process is governed by the internal diffusion.

The data presented in Fig. 6, are plotted according to Eq. (3), the result shown in Fig. 10, indicates that the control of internal diffusion still fitted the leaching data well at different liquid-to-solid ratios with the sulphuric acid concentration of 11 mol/dm³.

The data presented in Fig. 5 are plotted according to Eq. (3), the result is shown in Fig. 11. Fig. 7 indicates that the control of internal diffusion still fitted the leaching data well at different temperature with the sulphuric acid concentration of 11 mol/dm³. The apparent rate constants of the anatase acid leaching process were 0.00186, 0.00358, 0.00912, and 0.01561 at 60 °C, 80 °C, 100 °C, and 120 °C. According to the Arrhenius equation the plot of lnk versus 1/T was obtained as shown in Fig. 12. The apparent activation energy is 39.85 kJ/mol; this result verifies that the sulphuric acid leaching process of the anatase is controlled by the internal diffusion.

4.   Proposed schematic flowsheet

Based on the research mentioned above, the schematic flowsheet of the sulphuric acid leaching of the anatase is explored and tested are seen in Fig. 13. In this process, 500 g anatase with particle size of 75% at -74 μm was leached by sulphuric acid under the conditions of the liquid-to-solid ratio of 1/3 g/cm³,
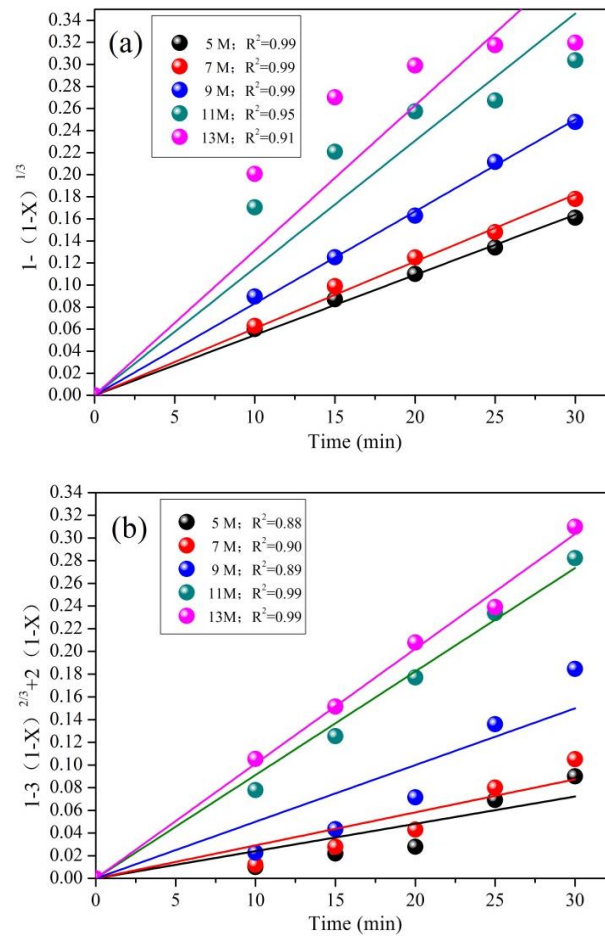
Fig. 9. Relationship between plots of $1-3(1-X)^{2/3}+2(1-X)$ (a) and $1-(1-X)^{1/3}$ (b) versus time at different initial sulphuric acid concentration
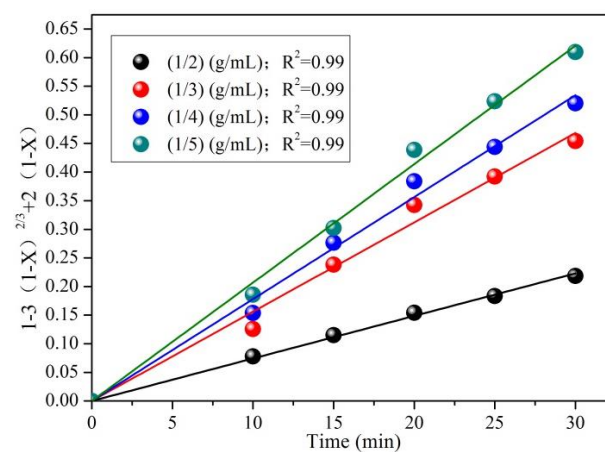

Fig. 10. Plots of $1-3(1-X)^{2/3}+2(1-X)$ versus time at different solid-to-liquid ratio

reaction temperature of 120 °C, initial acid concentration of 11 mol/dm^3, residence time of 30 min, and stirring speed of 200 rpm. Then, the obtained residue was leached once again under the conditions of the liquid-to-solid ratio of 1/3 g/cm^3, reaction temperature of 200 °C, initial acid concentration of 13 mol/dm^3, residence time of 30 min, and stirring speed of 200 rpm. The indexes of the process flow are presented in Table 2. The total leaching efficiency of TiO_2, Sc_2O_3, Al_2O_3, and Fe were 99.55%, 97.20%, 99.81%, and 99.91%, respectively. Comprehensive recovery of the metals from the pregnant leachate will be studied in future.

Moreover, the XRD patterns of the residues are shown in Fig. 14 indicating that the final leaching residue is of high purity silica, and being considered as the material of the silicon fertilizer.
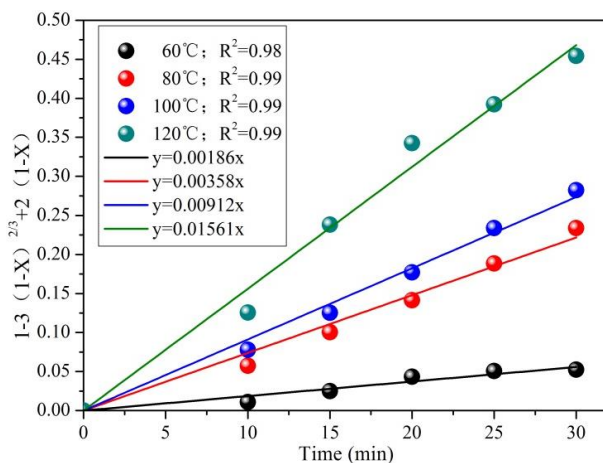

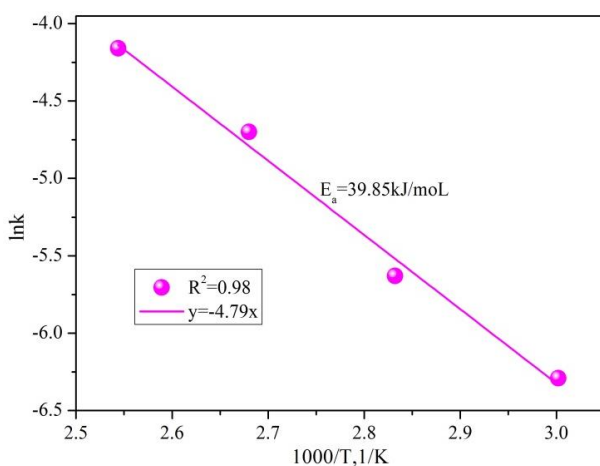Fig. 11. Plots of 1-3(1-X)$^{2/3}$+2(1-X) versus time at different reaction temperature
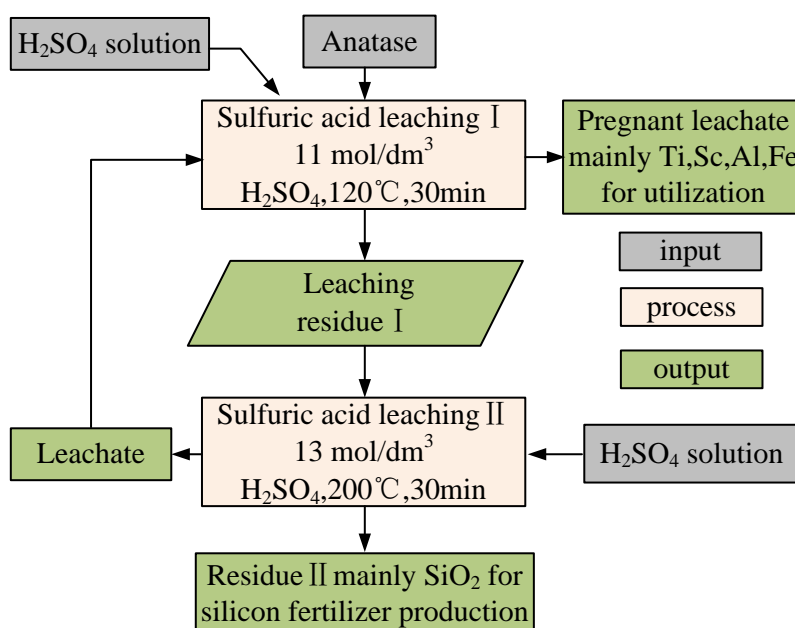

Fig. 12. Arrhenius plots for TiO$_2$ extractions

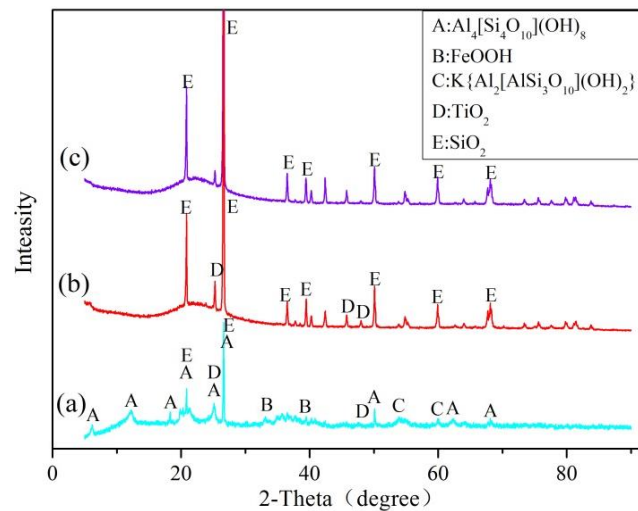Fig. 13. Schematic flowsheet of decomposition and leaching of titanium from anatase by H$_2$SO$_4$

Fig. 14. XRD patterns of the leaching residue, (a) raw anatase mineral, (b) acid leaching residue Ⅰ, (c) acid leaching residue Ⅱ

Table 2. The content in the solid phase and leaching rate of metals in different processes. Initially leaching with 11 mol/dm³ H₂SO₄ at 120 °C, followed by leaching with 13 mol/dm³ H₂SO₄ at 200 °C

Technological indexes	Fe		Al_2O_3		TiO_2		Sc_2O_3	
	Solid (%)	Leaching rate (%)	Solid (%)	Leaching rate (%)	Solid (%)	Leaching rate (%)	Solid (ppm)	Leaching rate (%)
Raw anatase	16.85	-	22.18	-	5.3	-	84.7	-
Leaching Ⅰ	0.40	99.31	3.92	94.98	2.43	85.04	21.5	90.60
Leaching Ⅱ	0.0056	87.59	0.17	96.15	0.082	97.01	7.5	70.23
Total leaching rate	-	99.91	-	99.81	-	99.55	-	97.20

5. Conclusions

With the increase of the acid concentration in the leaching solution, the boiling point of the leach liquor also increased. High sulphuric acid concentration and heating were used for the efficient leaching of titanium and other valuable metals from the anatase under atmospheric pressure. The results revealed that the leaching indexes increased with the increasing initial sulphuric acid concentration, reaction temperature, liquid-to-solid ratio, residence time, and with the decreasing the particle size. The initial sulphuric acid concentration and temperature were found to be the most significant parameters affecting the anatase leaching. Under the conditions of sulphuric acid concentration of 11 mol/dm³, leaching temperature of 120 ℃, agitation speed of 200 rpm, and solid-to-liquid ratio of 1/3 g/cm³, more than 90% titanium was leached within 30 min.

Of all the valuable metal elements in this ore, titanium is the most difficult to be leached. The leaching kinetics of titanium from the refractory anatase under atmospheric with sulphuric acid was studied for the first time. The anatase leaching kinetics were better described by the shrinking model, and is governed by was controlled by the diffusion of reactants through the residual layer. Both acid concentration and temperature were the most significant parameters for the titanium leaching efficiency. The apparent activation energy of titanium dioxide leaching from the refractory anatase by sulphuric acid solution was 39.85 kJ/mol.

The schematic flowsheet for comprehensively recovering the valuable metals from the anatase with sulphuric acid was explored and tested. Under appropriate two-stage countercurrent leaching conditions, over 99% TiO₂, 99% Al₂O₃, and 97% Sc₂O₃ were extracted respectively, and quartz was still remained in the residue. Promisingly, the final residue of high purity silica can be recycled to produce fertilizer in the future, which will be confirmed in our further study.

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