Study on the mechanism and kinetics of sulfuric acid leaching scandium from rich scandium anatase

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Abstract: Scandium and its compounds have excellent properties, and are widely used in cutting-edge fields such as optics, electronics, and alloys. Thus, scandium is an important strategic metal. However, scandium is extremely sparsely distributed in the earth's crust, rarely occurs as an independent mineral, and requires a complex recovery process. Therefore, the study of the extraction of scandium is of great practical significance. This study examined the leaching test and kinetics of scandium under the acid leaching system of refractory anatase ore. Under appropriate two-stage countercurrent leaching conditions, the first stage of the particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 ºC, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min; and the second stage of the initial H_2SO_4 concentration of 11 mol/L, leaching temperature of 150 ºC, acid/solid ratio of 4 ml/g, stirring speed of 300 rpm, and leaching time of 50 min, a scandium leaching rate of 96.98% was achieved. The kinetics of scandium leaching conformed to a shrinking-core model, and sulfuric acid concentration and temperature were the most important parameters affecting the scandium leaching rate. The kinetic analysis of scandium leaching at different sulfuric acid concentrations showed that as the concentration increased, the sulfuric acid leaching of scandium changed from being chemical reaction-controlled to internal diffusion-controlled, and the apparent reaction order was 1.2429. The kinetics of scandium leaching at different temperatures showed that the sulfuric acid leaching of scandium was reaction-controlled and the apparent activation energy was 42.21 kJ-mol^{-1}.

Keywords: anatase ore, sulfuric acid, leaching, kinetics, scandium

1. Introduction

Scandium (Sc) and its compounds have excellent mechanical and chemical properties, and are used to manufacture luminescent, laser, and magnetic materials as well as catalysts. Thus, they have become irreplaceable strategic resources in the fields of national defense, military, and high-tech applications (Li et al., 2017; Rivera et al., 2018). Sc is mainly distributed among other minerals in the form of associated minerals, and is usually recovered from the by-products of aluminum, tungsten, titanium, tin, uranium, and zirconium (Onghena et al., 2017; Ramasamy et al., 2018). Its extraction process is complex and exhibits a low recovery rate (Zhang et al., 2016), with an annual output of 10-15 tons only, while the current price of Scandia (Sc$_2$O$_3$) (99.99%) is US\$ 4600/kg (US Geological Survey, 2019). The lack of reliable supply and high production costs have hindered the application of Sc in high-end technology to a certain extent (Reid et al., 2017). Therefore, technological research on the extraction of Sc from different raw materials is of great practical significance.

Scandium oxide, a common and naturally occurring scandium compound, is insoluble in dilute acid and can only be dissolved at high temperatures in concentrated acid. The leaching rate of Sc directly affects its recovery rate; therefore, most studies on Sc recovery have focused on hydrometallurgical processes (Zhang and Edwards, 2013; Davris et al., 2017; Lebedev, 2003; Zakharov et al., 2011). Liu (Liu et al., 2017)the sulfation-roasting-leaching process was studied to selectively

dissolve scandium and REE in the red mud as rare earth sulfates, while reconverting other metal sulfates into corresponding oxides. Anawati (Anawati et al., 2019)the improvement in sulfate kinetics by direct acid baking by conventional heating at 200-400 ^oC for 1-2 hours proves that high-level extraction can be achieved by reducing reagent and water consumption. Acidic roasting has the advantage of co-extraction of impurities, especially iron, but the operating temperature in the water leaching step is high, and the extraction efficiency of scandium is moderate(Borra et al., 2016b, Liu et al., 2017).Jihye Kim (Kim and Azimi, 2020) developed a two-stage process was developed to recover scandium from laterite ore, carbothermic reduction process was performed at 1400–1600 ^oC using lignite as a reductant and calcia and/or silica as a fluxing reagent, scandium was successfully concentrated in the slag phase >14 times compared with that in the feed material, for NaOH cracking process, under the optimum conditions (high baking temperature, high NaOH ratio, long baking time, and low liquid ratio), 88% of the Sc was recovered from the slag. Ma (Shengfeng, 2012) studied the processes involved in the activated decomposition-HCl leaching of Sc from Bayan Obo tailings, wherein the Sc-bearing minerals were mainly riebeckite (containing 555g/t scandium) and jervisite (containing 190g/t scandium); they achieved a Sc leaching rate of 99.38% under the following conditions: an activator dose of 60%, roasting at 950 ^oC for 1.5 h, HCl concentration of 6 mol/L, solid to liquid ratio of 1:4, and acid leaching period of 6 h. Table 1 provides a summary of previous studies on the extraction of scandium by direct acid leaching.

Table1. Research on Sc Recovery in Hydrometallurgical Process

Resource	Sc concentration	Leaching agent	Leaching conditions	Sc recovery (%)	Reference
Fe-Ti residue	40–100 ppm	H_2SO_4	H_2SO_4 300 g/L,S/L = 1/7; 95 °C for 5hr. Samples were machined in: AGO-2U planetary-centrifugal activator; Pulverisette 5 planetary ball mill; Aktivator-2SLactivator.	85–95%	(Stepanov et al., 2018)
REE - silicate	0.006 wt%	H_2SO_4	H_2SO_4 dosage1.875 mL;15 h; 200 ^oC; 1/30	492µg/L	(Zhang et al., 2020)
Bayan Obo tailings	0.0085 wt%and 0.03 wt% (Sc2O3) beforeroasting-magnetic separation;	H_2SO_4	H_2SO_4:6–18 mol/L; 80–300 ^oC; S/L = 1/1–1/8.	96%	(B. Zhang et al., 2019)
Bauxite Residue	121 mg/kg	H_2SO_4+ H_2O_2	2.5 M H_2SO_4; 2.5 M H2O2; 90 ^oC; 30 min; S/L ratio 1/50	68%	(Alkan et al., 2018)
Nb ore concentrate	0.95 wt%	HCl	HCl 33%;S/L = 1/1.8–1/2.2; 60–100 ^oC;	97%	(Li et al., 2019)
Bauxite Residue	121 mg/kg	HCl	HCl 6 N; 24 h; 25 ^oC; S/L ratio 1/50	75–80%	(Borra et al.,2015b)

The leaching agents explored were sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), being the first the most common for industrial applications. (Li et al., 2019) It is reported that the leaching efficiency of HCl is higher than that of other inorganic acids, indicating that HCl has a strong high solubility for hydroxides. Because of the formation of scandium trichloride, the target element is easily separated from impurities during the entire leaching process (Zhang et al., 2013). For industrial applications, because hydrochloric acid has strong volatility, is highly corrosive to equipment and easily causes air pollution, it is preferable to use H_2SO_4 compared to HCl. (Stepanov et al., 2018, Zhang et al., 2013) The extraction of scandium from Fe sources was studied using different leaching agents. The results show that although the leaching agent is different, the recovery rate of scandium is almost the same, as high as 95%.(Borra et al.2015) evaluated the effects of different inorganic and organic acids on scandium leaching. Research results show that even at high temperatures, the efficiency of using organic acids is lower than that of inorganic acids. Sulfuric acid leaching can completely destroy the structure of silicate minerals, causing the target metal and silica to dissolve to form silica gel, which reduces the efficiency of scandium leaching. (Alkan et al.,2018) used Hydrogen oxide (H_2O_2) is used to inhibit silica gel. Another method, dry digestion, is also an effective method to inhibit the dissolution of amorphous silica from silicate. These methods have achieved higher extraction rate of one or two metals, the use of high operating temperature, prolong reaction time and involvement of multi-step processes are major limitations in the current processes (Purcell et al., 2020).

However, information is little available on the systematic kinetic study on Sc leaching from anatase using sulfuric acid leaching at normal pressure. In view of these, this paper aims to research Sc leaching from anatase. The effects of initial sulfuric acid concentration, leaching temperature, particle size, acid/solid ratio and stirring speed on the leaching of Sc were systematically investigated. Thermodynamic analysis, leaching kinetic calculations, and XRD and SEM-EDS analyses were performed to fully explain the sulfuric acid (H_2SO_4) leaching behavior of Sc. This process did not require pre-treatment of minerals, and offers the advantages of lower digestion temperature, faster kinetics during the acid leaching, and higher scandium extraction (96.98%).

2.   Materials and methods

2.1. Materials

The test samples were obtained from Sc-rich anatase ore in Qinglong, Guizhou, China. Chemical analysis of the elements in raw anatase was conducted by X-ray fluorescence spectroscopy (XRF, ZSX100e, Rigaku, Japan), and the results are presented in Table 2.

Table2. Results of chemical multi-element analysis

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 microstructure of the solid samples was studied in a scanning electron microscope (SEM, XL30ESEM-TM, Philips, Holland) equipped with energy dispersive spectrometer (EDS, EDAX Genesis, USA), phase analysis of the raw anatase and leached residue were investigated by XRD (XRD, D/Max 2200, Rigaku, Japan), the XRD results of the raw ore is shown in Fig. 1. The main minerals in the ore were anatase, limonite, quartz, kaolinite and sericite, which accounted for 95.60% of all the minerals. These were all weathered and altered minerals, with fine crystal sizes that were mostly less than 24μm, and exhibited mutually interspersed distribution, thus making monomeric dissociation challenging. No independent minerals of Sc were found in the ore. The Sc element was mainly found in kaolinite, sericite and other clay minerals (46.07%), and existed in the form of fine-grained inclusions or isomorphs. This was followed by limonite (33.25%) and anatase (13.64%), both in

the form of isomorphs. A large number of beneficiation tests have shown that due to the fine embedded particle size of anatase, enrichment through conventional methods of physical beneficiation is difficult, and can only be comprehensively recovered via chemical leaching methods. All experimental agents were of analytical reagent, sulfuric acid (ACS Reagent Grade, 98.0% Assay).
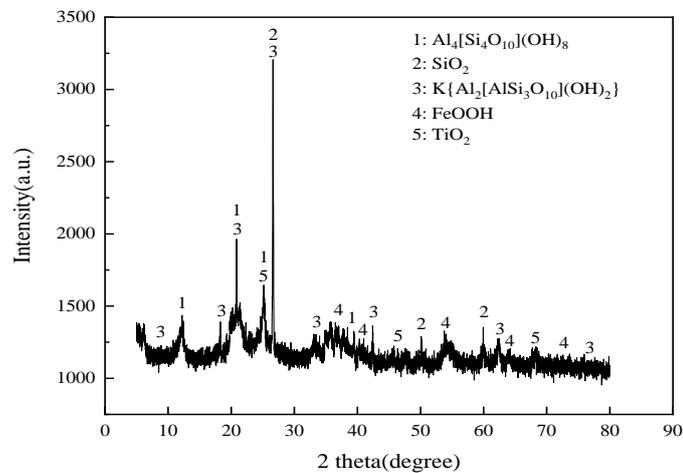
Fig. 1. XRD results of the raw ore

2.2. Methods

Leaching tests were performed in a self-made device. During the testing process, the leaching agent was first prepared according to the predetermined acidity and liquid-to-solid ratio and placed in a constant temperature oil bath for heating and stirring, while maintaining a given stirring speed. When the temperature of the leaching agent reached the required level for testing, the pre-prepared sample was added, and timing was started. The liquid level was maintained during the test to ensure a constant liquid-to-solid ratio. After the test, solid-liquid separation was performed using a vacuum filter. The equation of the Sc leaching rate is expressed as follows:

$$x = (1 - m_2 b / m_1 \alpha) \times 100\% \qquad (1)$$

where x is the leaching rate of Sc; m_1 is the mass of the sample (g); m_2 is the mass of the leaching residue (g); α is the content of Sc_2O_3 in the sample (wt.%); b is the content of Sc_2O_3 in the leaching residue (wt.%).

2.3. Analysis and testing

The composition of anatase and leaching residue was characterized by XRD, and the morphology of the sample was analyzed by scanning electron microscope (SEM, JEOL JSM-6510A, Japan) and field emission scanning electron microscope (FESEM, FEINova Nano SEM, USA).

3.　Results and discussion

3.1. Effect of initial H_2SO_4 concentration

H_2SO_4 concentration had a substantial effect on the leaching reaction; increasing the H_2SO_4 concentration accelerated the reaction rate of the leaching process, thus increasing the mineral leaching rate (Zhang et al., 2016). The effect of initial H_2SO_4 concentration on the leaching rate of the Sc_2O_3 was studied at the particle size of fraction of -0.074 mm 82.6%, leaching temperature of 80 ºC, acid/solid ratio of 3 ml/g, and stirring speed of 300 rpm. As shown in Fig. 2, the leaching rate of the Sc_2O_3 increased gradually with the H_2SO_4 concentration increase from 3 mol/L to 6 mol/L, after which there was a small increase with the further increase to 8 mol/L. Studies have shown that the dissolution of anatase greatly affected by acid concentration and temperature, high H_2SO_4 concentration should be selected for efficient leaching of valuable metals in the ore (Parhi et al., 2015).However, the elements of Sc, Ti, Al, Fe are known as low solubility in high sulfuric 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 is an effective metal hydrometallurgy technology, which can promote the leach reaction kinetics of the leaching process and obtain higher metal recovery by treating refractory ore (Kalinkin and Kalinkina, 2011; Ebadi and Pourghahramani, 2019). The corrosion effect of sulfuric acid on minerals gradually increased with the extension of the curing time and the increase of the curing temperature at the appropriate sulfuric acid dosage(Davris et al., 2016;Zhang et al., 2020). However, when the amount of acid exceeds the optimal concentration, the amount of free hydrogen ions in the leachate increases with the increase of sulfuric acid, and silica gel will be produced in the solution. Excessive acid will also cause environmental pollution and increase production costs(Zhang et al., 2020). The initial H_2SO_4 concentration was selected to be 6 mol/L.
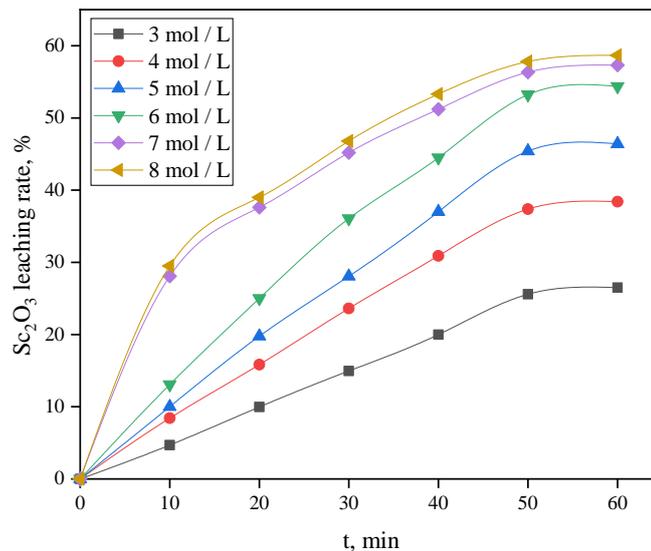
Fig. 2. Effect of initial H_2SO_4 concentration on the leaching of Sc_2O_3(particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 °C, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min)

3.2. Effect of temperature

Early exploration experiments show that the leaching rate of Sc_2O_3 by direct acid leaching can be boosted by improving the reaction temperature, more importantly, silica gel is formed in the leachate at a lower temperature, resulting in the inability of solids and liquids to separate (Gao et al., 2019). With an appropriate amount of sulfuric acid, as the temperature increases, the corrosion effect of sulfuric acid on minerals gradually increases, which promotes the decomposition of minerals, resulting in an increase in particle porosity, which is more beneficial to the leaching of Sc.As the H_2SO_4 concentration rises, the boiling point of the leach liquor increases, the boiling point of 6mol/L H_2SO_4 leachate is as high as about 107 °C. The effect of temperature on the leaching of Sc_2O_3 was investigated within the temperature range of 50 °C -100 °C at particle size of the fraction of -0.074 mm 82.6%, H_2SO_4 concentration of 6 mol/L, acid/solid ratio of 3 ml/g, and stirring speed of 300 rpm. As shown in Fig. 3, the leaching rate of the Sc_2O_3 efficiency increased significantly with the increase of temperature, particularly in the first 50 min. At 50 °C, only 15.25% Sc_2O_3 was leached then increased to 90.14% at 100 °C in 50 min. Therefore, the leaching temperature was set at 100 °C. Zhang (Zhang et al., 2020)use sulfuric acid solidification and water leaching treatment to extract scandium from silicate ore at 200 °C. The rare earth elements can be completely extracted into the solution by roasting the ore with concentrated sulfuric acid at 250-300 °C and then leaching with water (Li et al., 2004), Anawati&Azimi （Anawati&Azimi et al., 2019) explored the acid baking extraction of scandium from bauxite residues, and the scandium extraction reached the maximum efficiency (80%) at 400 °C. Rivera （Rivera et al.,2019） studied the improvement of sulfation kinetics by conventional heating at 200-400 °C for 1-2 hours by direct acid baking. Compared with the process, the temperature of the process has been significantly reduced.
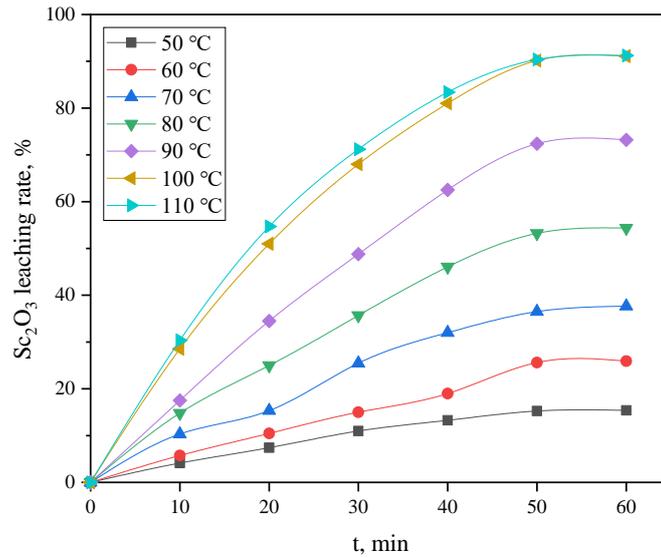
Fig. 3. Effect of temperature on the leaching of Sc_2O_3(particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 ºC, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min)

3.3. Effect of particle size

Mineral particle size usually affects the reaction by affecting the specific surface area of the particles. As the size of the mineral decreases, the specific surface area of the particles increases, and the contact area with the leachate increases, thereby accelerating the reaction (Luo et al., 2019). Increasing the fineness of grinding can increase the leaching speed. If the fineness of the grinding is too fine, it will not only increase the cost of grinding, but also increase the viscosity of the slurry, thereby increasing the diffusion resistance. In general, the decrease in the particle size of sample enhances the mineral dissolution (Zhang et al., 2011). The leaching experiments were performed in H_2SO_4 concentration of 6 mol/L, leaching temperature of 100ºC, leaching time 50min, acid/solid ratio of 3 ml/g, and stirring speed of 300 rpm using anatase samples with five different average particle sizes, viz., the fraction of -0.074 mm 52.4%,64.3%,75.1%,82.6%,91.3%. As shown in Fig. 4, the Sc_2O_3 leaching rate increased with a decrease in the particle size. When the grinding fineness is -0.074mm and the content is 82.6%, the
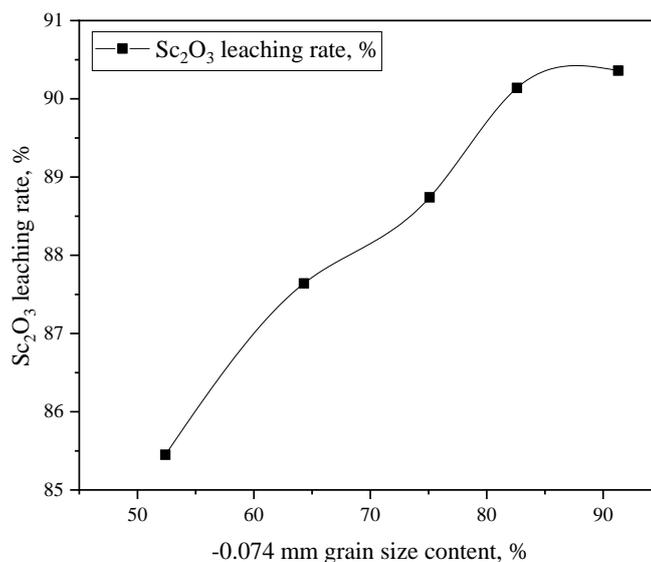
Fig. 4. Effect of -0.074 mm content of the feed on the leaching of Sc_2O_3(particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 ºC, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min)

scandium leaching rate reaches the maximum 78.21%; The larger specific surface area of the finer particles increased the interface reaction and effectively promoted the leaching reactions, then reducing the particle size, the improvement of the leaching rate is not obvious, and it is difficult to grind the too fine particle size. The particle size of the fraction of -0.074 mm 82.6% was kept in the subsequent tests.

3.4. Effect of acid/solid ratio

The liquid-to-solid ratio indicates the ratio of the volume of the leaching agent to the mass of the ore in the leaching system. On the one hand, the liquid-to-solid ratio determines the amount of sulfuric acid used in the leaching process, on the other hand, it directly affects the leaching rate of valuable elements in the ore, the viscosity of the system, the concentration of metal ions, and the stirring resistance. Some studies have shown that increasing the liquid/solid mass ratio properly can promote the mass transfer process at the solid–liquid interface (Aydogan et al., 2005, Zhang et al., 2005).The effect of acid/solid ratio on the leaching of Sc_2O_3 was investigated with the other parameters were set as follows: the particle size of the fraction of -0.074 mm 82.6%, H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 °C, and stirring speed of 300 rpm. The result is shown in Fig. 5. When the acid/solid ratio was 3ml/g, the Sc_2O_3 leaching rate reached 90.14% in 50 min; when the liquid–solid ratio increased from 3 mL/g to 4 mL/g, the leaching efficiency changed little perhaps indicating the value reached is quite near to the extraction limit. The liquid–solid ratio mainly affected leaching in two ways. Increasing the liquid–solid ratio increased the relative amounts of sulfuric acid to solids added, which increased leaching efficiency. Increasing the liquid–solid ratio also decreased the viscosity of the reaction system, which improved the mass transfer of the leaching reaction(Luo et al., 2019). However, increasing the liquid–solid ratio will also increase the leaching cost, therefore, the acid/solid ratio of 3ml/g was selected.
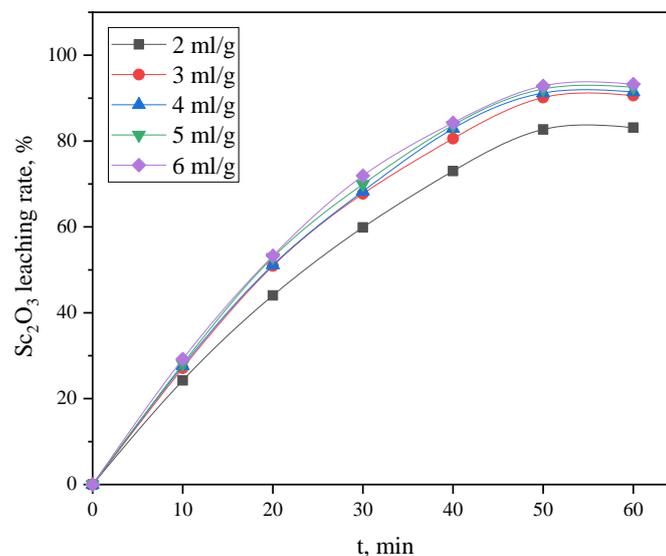
Fig. 5. Effect of acid/solid ratio on the leaching of Sc_2O_3 (particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 °C, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min)

3.5. Effect of stirring speed

Stirring during the leaching operation can strengthen the relative movement of the two phases of the mineral particles and the leaching agent, reduce the concentration difference between the two sides of the liquid film layer on the surface of the mineral particles, and improve the leaching reaction product from the inside of the mineral particle through the liquid film layer to the leaching solution, diffusion speed, so as to accelerate the speed of diffusion outside the leaching reaction process, at the same time, stirring can also strengthen the heat transfer between the liquid and the solid wall, and make the

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material heated evenly.The effect of stirring speed on the Sc_2O_3 leaching rate was investigated for stirring speed of 100, 200, 300, 400, and 500 rpm under the following conditions: the particle size of the fraction of -0.074 mm 82.6%, H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 °C, and acid/solid ratio of 3ml/g. The result is shown in Fig. 6. The leaching efficiency of the Sc_2O_3 increased with stirring speed increased, from 81.69% to 90.14 % on increasing the stirring speed from 100 rpm to 300 rpm. The leaching efficiency did not significantly change with further increasing in stirring speed, this could be accounted for by the reason that increasing the stirring speed can promote the internal diffusion of oxygen in the leachate and the suspension of mineral particles (Qin et al., 2011), **the leaching reaction of Sc_2O_3 is no longer affected by external diffusion**, so an appropriate stirring speed was selected as 300 rpm.
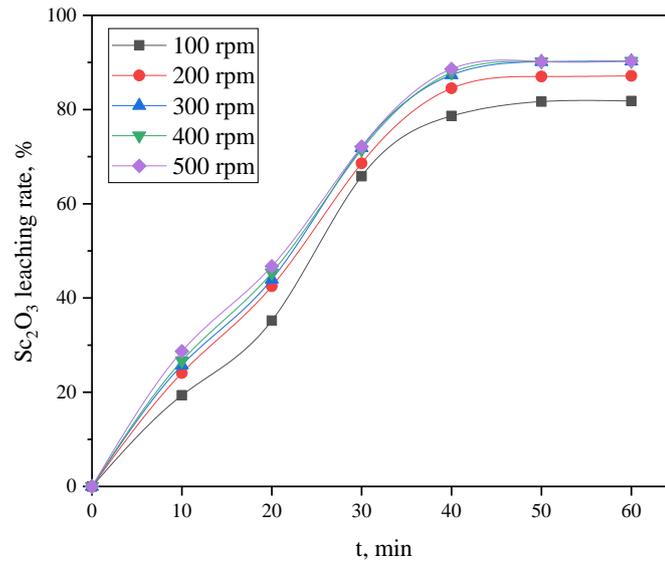
Fig. 6. Effect of stirring speed on the leaching of Sc_2O_3 (particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching temperature of 100 °C, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min)

3.6. The second stage of sulfuric acid leaching

The leaching residue obtained under optimal leaching process conditions was used as the ore sample for the second stage of sulfuric acid leaching. The other parameters were set as follows: initial H_2SO_4 concentration of 11 mol/L, leaching temperature of 150 °C, acid/solid ratio of 4 ml/g, and stirring speed of 300 rpm. The results are shown in Table 3.

Table 3. The content in the solid phase and leaching rate of metals in different processes

Technological indexes	Sc_2O_3		TiO_2		TFe		Al_2O_3	
	grade (ppm)	Leaching rate (%)	grade (%)	Leaching rate (%)	grade (%)	Leaching rate (%)	grade (%)	Leaching rate (%)
Raw anatase	84.7	--	5.30	--	16.85	--	22.18	--
Leaching I	21.5	90.14	8.33	38.70	1.52	96.66	12.08	80.27
Leaching II	7.5	96.98	0.56	96.40	0.046	99.90	0.12	99.73

The results show that when anatase ore was only subjected to a one-stage leaching process with sulfuric acid, then under optimal leaching conditions, the leaching rates of Sc, Fe, and Al were relatively high, whereas that of Ti was low. During the leaching process, it was only when the main

minerals in the ore were completely dissolved that the enveloped Sc within could be exposed to the medium and be extracted. The results of the leaching test indicate that Sc in kaolinite, sericite, and limonite was more readily leached, while Sc leaching in anatase was relatively more difficult. The second stage of sulfuric acid leaching enabled the efficient leaching of anatase from the first-stage leaching residue, while significantly increasing the leaching rate of titanium. According to the results of process mineralogy, the distribution rate of Sc in anatase was 13.64%, and Sc could only be leached completely when anatase was leached efficiently, i.e. when the leaching rate of titanium was high.

Borra(Borra et al.,2016) processed bauxite residues by direct acid leaching. The recovery rate of rare earth ore was in the range of 70-80%. At the same time, aluminum, silicon and titanium were dissolved during leaching. In another study(Alkan et al.,2018), a combination of hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) was used as the leaching solution to be leached at 90 ^oC for 30 minutes to avoid the polymerization of silica and to achieve about 70% of the scandium being extracted; in order to further improve Leaching efficiency, the novel process of "H_2SO_4 leaching-with microwave pretreatment" is used to recover rare earth elements; (Onghena et al., 2017; Xia et al., 2015; Zhu et al., 2012) the concentration of REE in the leaching solution is increased through multi-stage treatment. This method reduces acid consumption and increases the metal leaching rate; (Rivera et al.,2016) two-step treatment of bauxite residues through dry digestion and subsequent water leaching improves the extraction rate of rare earth elements while preventing silica polymerization; in another study(Alkan et al.,2018), red mud was subjected to dry digestion treatment, Sc is selectively recovered by suppressing the dissolution of Ti and Si. (Ochsenkuehn-Petropoulou et al.,2018)The selective recovery of scandium leached using H_2SO_4 as the leaching agent, the recovery rate of scandium is improved through multi-step leaching. Compared with the above process, this process does not require pretreatment of minerals, has a lower temperature, does not need to be classified in the extraction process, and does not need to add fluoride ions, hydrogen peroxide and other improvements during the leaching process, the scandium leaching rate is higher during the leaching process. Although scandium is the target element, it can also extract titanium, iron, aluminum and silicon while extracting scandium. The extracted elements can be used for new product development to achieve comprehensive utilization of resources.

3.7. Mechanisms of Sc leaching

3.7.1. Thermodynamic basis of the leaching reaction

To facilitate the analysis, the leaching reactions were categorized into the sulfuric acid leaching reactions of the four main Sc-bearing minerals (kaolinite, sericite, limonite and anatase), and the sulfuric acid dissolution reaction of Sc.

3.7.2. Scandium dissolution reaction

Because the elemental composition of Sc is very complex and it does not exist in the form of an independent mineral, scandium oxide was used to replace the mineral composition of Sc for the analysis and calculation of the scandium dissolution reaction. The reaction is expressed by Eq. (2), and the standard equilibrium constant for calculating the reaction K^θ is shown in Table 4.

$$Sc_2O_3 + 3H_2SO_4 \rightarrow Sc_2(SO_4)_3 + 3H_2O \tag{2}$$

Table 4. Standard equilibrium constant of scandium dissolution reaction

Temperature (K)	$\Delta_r G_m^\theta$ (kJ/mol)	lnK^θ	K^θ
298.15	-340.26	137.27	4.13×10^{59}
323.15	-344.43	128.20	4.75×10^{55}
348.15	-348.85	120.52	2.19×10^{52}
373.15	-351.25	113.22	1.48×10^{49}

3.7.3. Kaolinite dissolution reaction

The dissolution reaction of kaolinite in an acidic solution is expressed by Eq. (3), and the standard equilibrium constant for calculating the reaction K^θ is shown in Table 5.

$$Al_4[Si_4O_{10}](OH)_8 + 6H_2SO_4 \rightarrow 2Al_2(SO_4)_3 + 4H_4SiO_4 + 10H_2O \qquad (3)$$
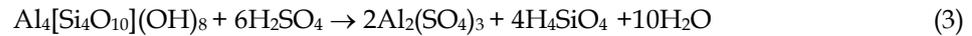
Table 5. Standard equilibrium constant of kaolinite dissolution reaction

Temperature (K)	$\Delta_r G_m^\theta$ (kJ/mol)	lnK^θ	K^θ
298.15	-6712.58	2707.97	∞
323.15	-6711.81	2498.19	∞
348.15	-6713.10	2319.24	∞
373.15	-6716.63	2165.00	∞

3.7.4. Sericite dissolution reaction

The dissolution reaction of sericite in an acidic solution is expressed by Eq. (4), and the standard equilibrium constant for calculating the reaction K^θ is shown in Table 6.

$$2K\{Al_2[AlSi_3O10](OH)_2\} + 7H_2SO_4 + H_2O \rightarrow 2Al_2(SO_4)_3 + K_2SO_4 + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4 \qquad (4)$$

Table 6. Standard equilibrium constant of sericite dissolution reaction

Temperature (K)	$\Delta_r G_m^\theta$ (kJ/mol)	lnK^θ	K^θ
298.15	-127.37	51.38	2.06×10^{22}
323.15	-113.04	42.08	1.87×10^{18}
348.15	-98.42	34.00	5.83×10^{14}
373.15	-84.00	27.07	5.73×10^{11}

3.7.5. Limonite dissolution reaction

The dissolution reaction of limonite in an acidic solution is expressed by Eq. (5), and the standard equilibrium constant for calculating the reaction K^θ is shown in Table 7.

$$2FeO(OH) + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 4H_2O \qquad (5)$$
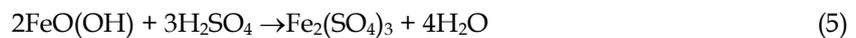
Table 7. Standard equilibrium constant of limonite dissolution reaction

Temperature (K)	$\Delta_r G_m^\theta$ (kJ/mol)	lnK^θ	K^θ
298.15	-79.11	13.85	1.04×10^{106}
323.15	-74.86	12.10	1.80×10^{105}
348.15	-70.81	10.62	4.09×10^{104}
373.15	-67.02	9.38	1.18×10^{104}

3.7.6. Anatase dissolution reaction

The dissolution reaction of anatase in an acidic solution is expressed by Eq. (6):

$$TiO_2 + 2H^+ \rightarrow TiO^{2+} + H_2O \tag{6}$$

The standard molar Gibbs free energy of formation $\Delta_r G_m^\theta$ for the relevant substances at T = 298.15 K is available in the Thermodynamics Handbook, and the data are as follows: -883.30 kJ/mol for $TiO_2(s)$, 6.24 kJ/mol for $H^+(aq)$, -138.00 kJ/mol for $TiO^{2+}(aq)$, and -306.68 kJ/mol for $H_2O(l)$. The calculations showed that $\Delta_r G_m^\theta$ =426.14 kJ/mol>0; hence, the dissolution reaction could not proceed spontaneously. Owing to the lack of relevant thermodynamic data in high temperature conditions, further investigation is required to elucidate the thermodynamics of the sulfuric acid dissolution reaction of anatase under high temperature conditions. Relevant experimental studies have also shown that the leaching of anatase can only be carried out completely under higher concentrations of sulfuric acid and increased reaction temperatures (Georgiou and Papangelakis, 1998).

The results of the thermodynamic analysis and calculations above indicate that the sulfuric acid leaching of Sc is theoretically feasible. According to the standard equilibrium constants of the dissolution reaction between the various minerals and sulfuric acid, kaolinite was the easiest mineral to leach, followed by sericite and limonite, whereas anatase was relatively difficult to leach. The thermodynamics of leaching can be used to determine the theoretical feasibility of leaching reactions, as well as the direction and limits of the reactions. However, in reality, leaching reactions between Sc-bearing minerals and sulfuric acid cannot take place easily. Therefore, studying the kinetics of leaching is necessary.

3.7.7. Kinetic analysis

We can see from the analysis above that the contents of kaolinite, sericite, and quartz accounted for the majority of the total mineral composition. During the sulfuric acid leaching process of anatase, quartz did not react with sulfuric acid; meanwhile, kaolinite and sericite did not dissolve completely when reacting with sulfuric acid, but instead left a layer of inert residue, which caused the leaching process to follow a shrinking-core model for the inert residue layer (Georgiou and Papangelakis, 1998; Levenspiel, 1999). As the leaching process took place under high-speed mechanical stirring, the effect of liquid film diffusion was excluded. Therefore, there were two possible kinetic control models for the sulfuric acid leaching process of anatase.

- Kinetic equation for chemical reaction-controlled leaching:

$$1 - (1-x)^{1/3} = k_x t \tag{7}$$

- Kinetic equation for internal diffusion-controlled leaching:

$$1 - 3(1-x)^{2/3} + 2(1-x) = k_x t \tag{8}$$

where x is the extraction efficiency of scandium at time t (min), k_x is the apparent reaction rate (min^{-1}).

The apparent reaction orders for the sulfuric acid leaching reaction of anatase are expressed by Eq. (9):

$$\left(\frac{dx}{dt}\right)_1 \Big/ \left(\frac{dx}{dt}\right)_2 = \left(\frac{c_{01}}{c_{02}}\right)^n \tag{9}$$

Taking the logarithm of this equation and plotting it against lnk-lnC_0, a straight line was obtained, the slope of which represented the apparent reaction order n.

The reaction rate constant K was a function of temperature, and the effect of temperature on it can be expressed by the Arrhenius formula Eq. (10) (Aquilanti et al., 2010).

$$ln k_x = lnA - E_a / RT \tag{10}$$

where A is the frequency factor, E_a is the apparent activation energy (J·mol^{-1}), R is the gas constant (8.314 J·mol^{-1}·K^{-1}) and T (K) is absolute temperature.

The data presented in Fig. 2, are plotted according to Eq. (7) and Eq. (8) respectively, the results are shown in Fig. 7 (a) and (b). When the H_2SO_4 concentration was 3 mol/L-6 mol/L, $1 - (1-x)^{1/3}$ showed a good linear relationship with time t, which suggests that when the H_2SO_4 concentration was within the range of 3mol/L-6mol/L, the leaching of sulfuric acid from anatase was under chemical

reaction control. At this point, increasing the H_2SO_4 concentration and raising the leaching temperature could improve the reaction rate of leaching, thus indicating that the reaction rate of Sc-bearing minerals with sulfuric acid plays a major role in reaction-controlled leaching. When the H_2SO_4 concentrations were 7 mol/L and 8 mol/L, $1 - 3(1 - x)^{2/3} + 2(1 - x)$ showed a good linear relationship with time t, suggesting that at H_2SO_4 concentrations of 7mol/L and 8mol/L, the leaching reaction was under internal diffusion control, and the diffusion rate of liquid products through the inert residue layer played a major role in controlling the rate of the leaching reaction. At this point, increasing the concentration of H_2SO_4 no longer affected the rate of the leaching reaction significantly. Effective methods, such as increasing the temperature, are required to reduce the thickness of the inert residual layer and thus increase the reaction rate of the leaching process.

The apparent rate constants of the anatase acid leaching process were 0.00187, 0.00289, 0.00363, and 0.00447 at 3 mol/L、4 mol/L、5 mol/L and 6 mol/L. According to the Eq. (9) the plot of lnk versus lnC was obtained as shown in Fig. 8, the apparent reaction order is 1.2429. According to the leaching kinetics, when the reaction order is greater than 1, increasing the concentration of the leaching solution changes the leaching reaction mechanism from being influenced by a chemical reaction control to an internal diffusion control. This indicates that when the H_2SO_4 concentration is increased to 7 mol/L, the leaching reaction mechanism changes from being under a chemical reaction control to an internal diffusion control.
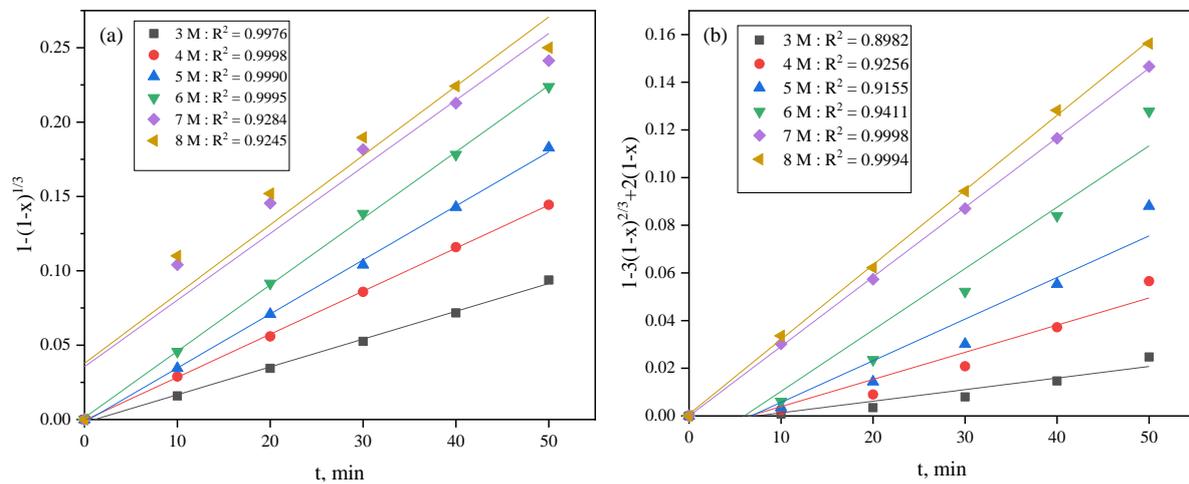
Fig. 7. Relationship between plots of $1 - (1 - x)^{1/3}$ (a) and $1 - 3(1 - x)^{2/3} + 2(1 - x)$ (b) versus time at different initial H_2SO_4 concentration
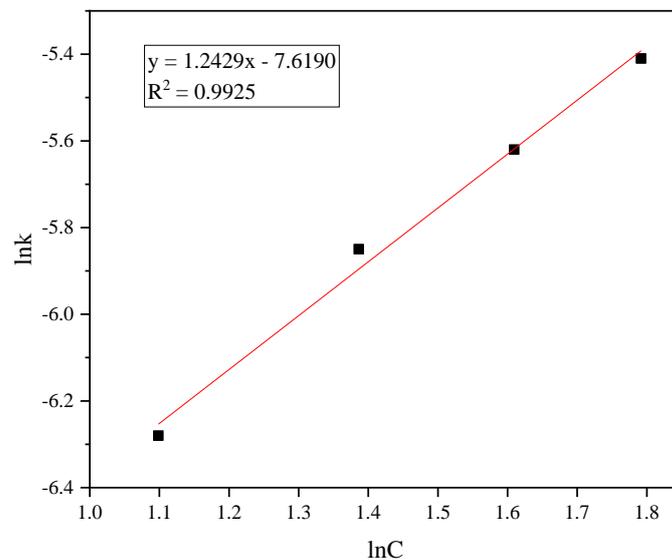
Fig. 8. The relationship between the leaching rate of Sc_2O_3 and H_2SO_4 concentration

The data presented in Fig. 3 are plotted according to Eq. (7), the result is shown in Fig. 9. Fig. 9 indicates that the control of chemical reaction still fitted the leaching data well at different temperature with the H_2SO_4 concentration of 6 mol/L. The apparent rate constants of the anatase acid leaching process were 0.00108, 0.0018, 0.00285,0.00448,0.00704,0.01072 and 0.01093 at 50 °C, 60 °C, 70 °C, 80 °C ,90 °C, 100 °C and 110 °C. According to the Eq. (10) the plot of lnk versus 1000/T was obtained as shown in Fig. 10, the apparent activation energy is 42.21 kJ·mol⁻¹. According to the leaching theory, when the apparent activation energy exceeds 42 kJ·mol⁻¹, the rate-controlling step of the leaching reaction represents the chemical reaction. The calculation of apparent activation energy further proves that the sulfuric acid leaching process of anatase is reaction-controlled. When controlled by the chemical reaction step, the reaction rate increases sharply with the increase in temperature, and temperature has a significant impact on the reaction rate. When controlled by diffusion, the reaction rate is accelerated by the increase in temperature, but the effect of temperature on the reaction rate is less significant than when the process is reaction-controlled.

The data presented in Fig. 5, are plotted according to Eq. (7), the result shown in Fig. 11, indicates that the control of chemical reaction still fitted the leaching data well at different acid/solid ratio with the H_2SO_4 concentration of 6 mol/L.
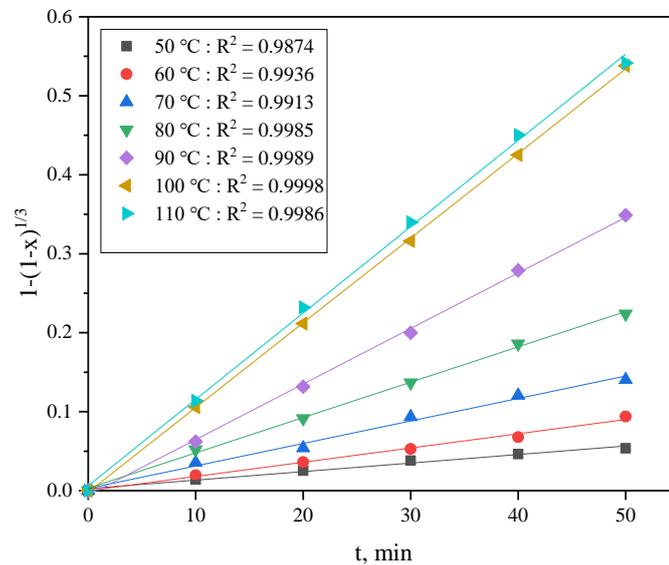
Fig. 9. Plots of $1 - (1-x)^{1/3}$ versus time at different reaction temperature
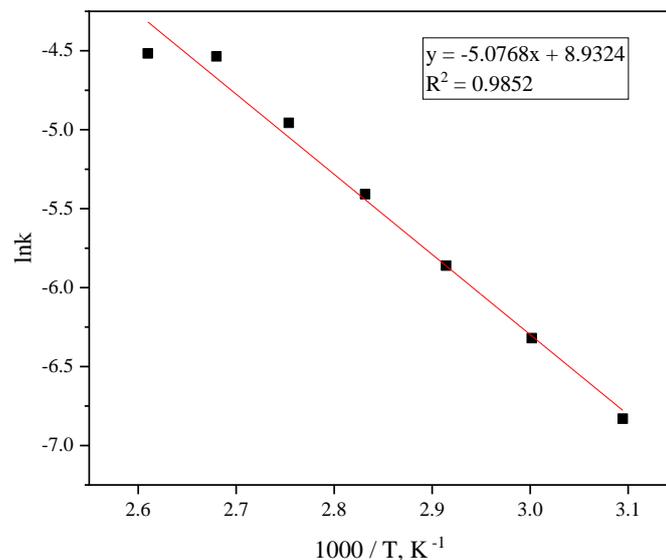
Fig. 10. Arrhenius plots for Sc_2O_3 leaching rate
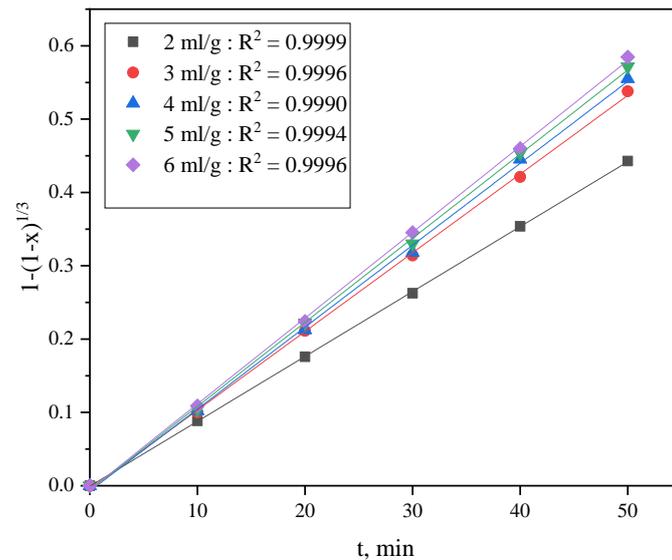
Fig. 11. Plots of $1 - (1 - x)^{1/3}$ versus time at different acid/solid ratio

3.8.   Analytical testing of raw ore and leaching residue

3.8.1. XRD analysis

The physical phase changes during the leaching process can be determined by XRD analysis, and the results in Fig. 12 showed that the main mineral phases in the first-stage leaching residue were SiO_2 and anatase; the diffraction peaks of anatase were prominent, while the diffraction peaks of kaolinite, limonite, and sericite disappeared. This indicates that the leaching reactions of kaolinite, limonite, and sericite with sulfuric acid were carried out thoroughly, whereas that of anatase with sulfuric acid was more difficult to carry out. In addition, the appearance of SiO_2 and anatase phases indicates that the relative contents of SiO_2 and anatase increased during the leaching process, which is manifested by the higher contents of TiO_2 and SiO_2 in the first-stage leaching residue than that in the raw ore. The main mineral phase in the second-stage leaching residue was SiO_2, while that of anatase disappeared, indicating that the leaching reaction between anatase and sulfuric acid was complete in the second stage of the sulfuric acid leaching process.
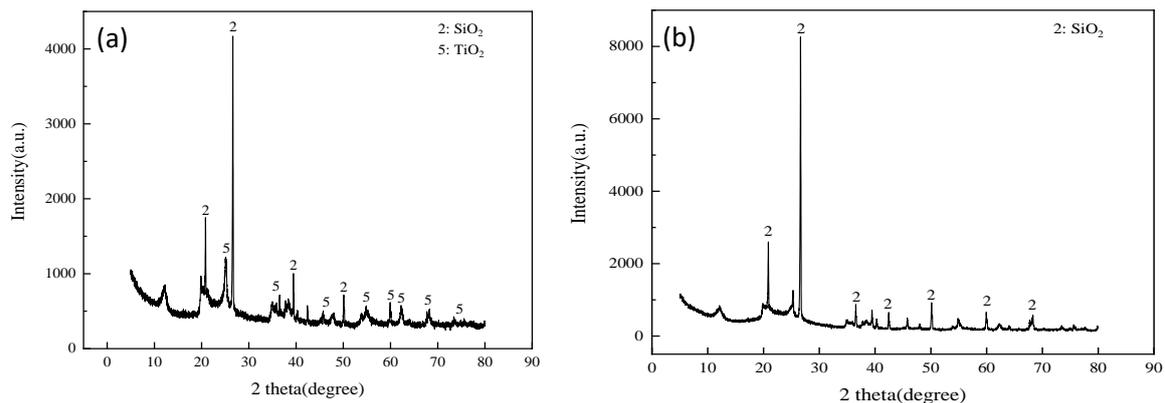
Fig. 12. XRD analysis of leaching residue, (a)XRD results of the first stage leaching residue, (b)XRD results of the second stage leaching residue

3.8.2. SEM-DES analysis

SEM-DES analysis can be used to determine the morphological and compositional changes that occur during the leaching process. The results in Fig. 13 showed that the raw ore structure is relatively dense, and the dissemination relationship between the various minerals is complex. In the first-stage leaching residue, the structure became somewhat loose and porous, while in the second-stage leaching

residue, the structure became looser and sponge-like. These observations indicate that, during the leaching process, the minerals were not completely dissolved, but left a residue layer that was insoluble in sulfuric acid. According to the results of process mineralogy, the main minerals involved in the sulfuric acid leaching process were kaolinite, limonite, sericite and anatase, and the content of kaolinite was very high, accounting for nearly half of the total composition. Among them, limonite and anatase were completely dissolved by the reaction with sulfuric acid and disappeared, whereas kaolinite and sericite were not completely dissolved and left a SiO_2 layer that was insoluble in sulfuric acid, thereby causing the grain structure of the ore to become loose and porous.

According to the EDS analysis results, seen in Fig. 14, the elemental peaks of A1 and Fe disappeared in the first-stage leaching residue, indicating that the minerals containing A1 and Fe (kaolinite, limonite, sericite, etc.) had reacted with sulfuric acid and dissolved, whereas the elemental peak of Ti was still present; this result implied that the leaching reaction between Ti-containing anatase and sulfuric acid was incomplete. The elemental peak of Ti disappeared in the second-stage leaching residue, indicating that the leaching reaction between Ti-containing anatase and sulfuric acid was complete in the second stage of the sulfuric acid leaching process and that the Ti element dissolved into the leaching solution.
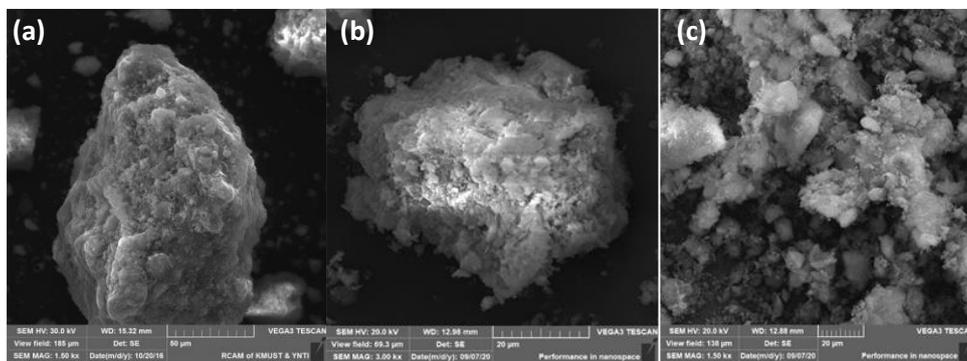
Fig. 13. Morphology of the anatase samples, (a) SEM images of the raw ore, (b) SEM images of the first stage leaching residue, (c) SEM images of the second stage leaching residue
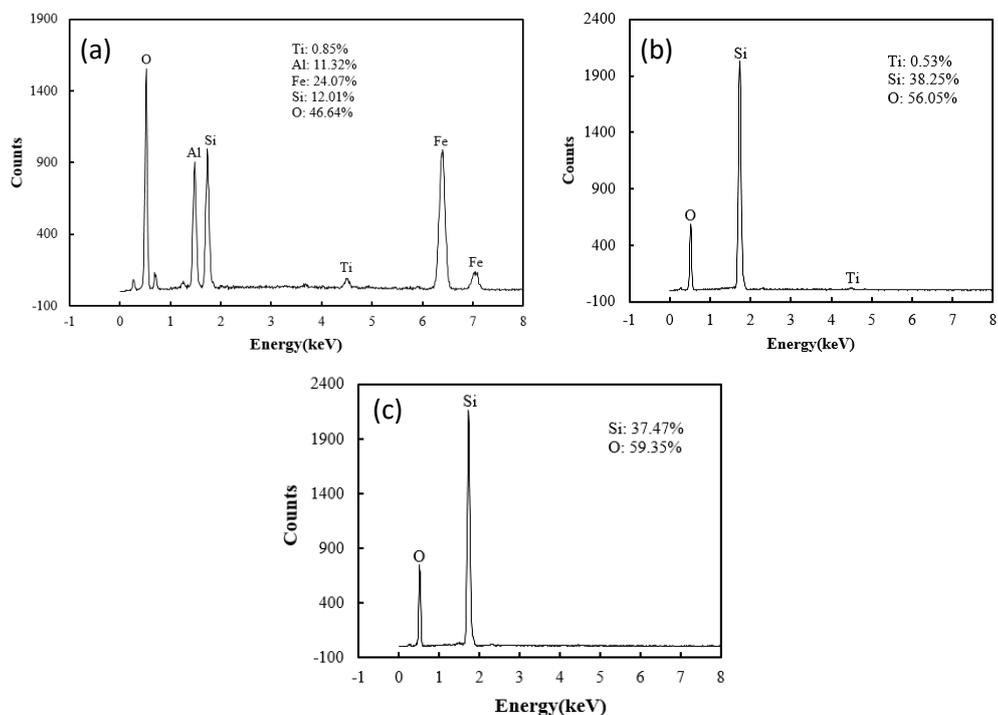
Fig. 14. EDS patterns of the anatase samples, (a) EDS results of the raw ore, (b) EDS results of the first stage leaching residue, (c) EDS results of the second stage leaching residue

4. Conclusions

Through Sc leaching tests, the following process conditions were observed to be optimum for Sc leaching: particle size of fraction of -0.074 mm 82.6%, initial H_2SO_4 concentration of 6 mol/L, leaching, temperature of 100 ^oC, acid/solid ratio of 3 ml/g, stirring speed of 300 rpm, and leaching time of 50 min. The leaching rates of the main elements in the first stage of leaching were 90.14% for Sc, 38.70% for Ti, 96.66% for Fe and 80.27% for Al. Exploratory testing of two-stage sulfuric acid leaching resulted in the efficient leaching of anatase from the leaching residue under optimal leaching process conditions, and the leaching rate of Sc was greatly improved.

The results of the thermodynamic analysis and calculations show that when the four main Sc-bearing minerals in Sc-rich anatase ore were subjected to the leaching reaction with sulfuric acid, kaolinite was easily the most leached, followed by sericite and limonite; however, leaching was more difficult in anatase. The results of the leaching kinetic test under different H_2SO_4 concentrations showed that as the concentration of H_2SO_4 increased, the process of sulfuric acid leaching from Sc-rich anatase ore changed from chemical reaction control to internal diffusion control, and the apparent reaction order was 1.2429. The results of the leaching kinetic test under different temperatures showed that the process of sulfuric acid leaching from Sc-rich anatase ore was reaction-controlled, and the apparent activation energy of the leaching reaction was 42.21 kJ·mol^{-1}. XRD analysis showed that the main mineral phases in the first-stage leaching residue were SiO_2 and anatase, and the main mineral phase in the second-stage leaching residue was SiO_2. SEM-EDS analysis showed that as the leaching process progressed, limonite and anatase reacted with sulfuric acid, thus dissolving completely and disappearing. Conversely, kaolinite and sericite did not dissolve completely, but instead left an insoluble layer of SiO_2, causing the grain structure of the ore to be loose and porous.

Acknowledgments

References

AYDOGAN, S., ARAS, A ., CANBAZOGLU, M., et al., 2005. *Dissolution kinetics of sphalerite in acidic ferric chloride leaching*.J. Chemical Engineering Journal. 114(1-3), 67-72.

AQUILANTI, V., MUNDIM, K. C., ELANGO, M., KLEIJN, S., KASAI, T., 2010. *Temperature dependence of chemical and biophysical rate processes, Phenomenological approach to deviations from Arrhenius law.* Chem. Phys. Lett. 498, 209–213.

ANAWATI, J., GISELE., et al., 2019. *Recovery of scandium from Canadian bauxite residue utilizing acid baking followed by water leaching – ScienceDirect*.J. Waste Management. 95, 549-559.

ALKAN, G ., YAGMURLU, B ., CAKMAKOGLU, S ., et al., 2018. *Novel Approach for Enhanced Scandium and Titanium Leaching Efficiency from Bauxite Residue with Suppressed Silica Gel Formation*.J. Scientific Reports. 8(1), 5676.

ALKAN, G ., YAGMURLU, B ., GRONEN, L ., et al., 2019. *Selective silica gel free scandium extraction from Iron-depleted red mud slags by dry digestion*.J.. Hydrometallurgy, 185.

BORRA, C, R, PONTIKES, Y, BINNEMANS, K, VAN, GERVEN, T. et al., 2015.*Leaching of rare earths from bauxite residue (red mud)*. Miner Eng 76, 20–27.

BORRA, C, R ., et al., 2016.*Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching*. J. Minerals Engineering. 92, 151-159.

DAVRIS, P., STOPIC, S., BALOMENOS, E., PANIAS, D., PASPALIARIS, I., FRIEDRICH, B., 2017. *Leaching of rare earth elements from eudialyte concentrate by suppressing silica gel formation*. Miner. Eng. 108, 115–122.

EBADI, H., POURGHAHRAMANI, P., 2019. *Effects of mechanical activation modes on microstructural changes and reactivity of ilmenite concentrate.* Hydrometallurgy 188, 38–46.

GAO, L., RAO, B., DAI, H., et al., 2019. *Kinetics of sulphuric acid leaching of titanium from refractory anatase under atmospheric pressure.* Physicochem. Probl. Miner. Process. 55, 467–478.

GEORGIOU, D., PAPANGELAKIS, V. G., 1998. *Sulphuric acid pressure leaching of a limonitic laterite, Chemistry and kinetics.* Hydrometallurgy 49, 23–46.

PURCELL, W., SINHA, M. K., VILAKAZI, A. Q., NETE, M., 2020. *Selective precipitation study for the separation of iron and titanium from ilmenite*. Hydrometallurgy 191, 105242.

KALINKIN, A. M., KALINKINA, E. V., 2011. *Modelling of the sulphuric acid leaching of mechanically activated titanite*. Hydrometallurgy 108, 189–194.

KIM, J., AZIMI, G., 2020. *An innovative process for extracting scandium from nickeliferous laterite ore, Carbothermic reduction followed by NaOH cracking.* Hydrometallurgy 191, 105194.

LEBEDEV, V. N., 2003. *Sulfuric acid technology for processing of eudialyte concentrate.* Russ. J. Appl. Chem. 76, 1559–1563.

LEVENSPIEL, O., 1999. *Chemical reaction engineering*. Ind. Eng. Chem. Res. 38, 4140–4143.

LIU, Z ., ZONG, Y ., LI, H, X., et al., 2017. *Selectively recovering scandium from high alkali Bayer red mud without impurities of iron, titanium and gallium*. J. Rare Earths, 35(009), 896-905.

LI D ., YONG, Z ., MENG, S., et al., 2004.*Separation of thorium(IV) and extracting rare earths from sulfuric and phosphoric acid solutions by solvent extraction method*.J. Journal of Alloys and Compounds.374(1–2), 431-433.

LI, C., LIANG, B., GUO, L. H., 2007. *Dissolution of mechanically activated Panzhihua ilmenites in dilute solutions of sulphuric acid.* Hydrometallurgy 89, 1–10.

LI, H., CAO, F., GUO, S., NING, Z., LIU, Z., JIA, Y., et al., 2017. *Microstructures and properties evolution of spray-deposited Al-Zn-Mg-Cu-Zr alloys with scandium addition.* J. Alloys Compd. 691, 482–488.

LI, S, C ., KIM, S ,C ., KANG, C, S., 2019.*Recovery of scandium from KOH sub-molten salt leaching cake of fergusonite*. J. Minerals Engineering, 137, 200-206.

LUO Y , X., CHEN, Z, Z., et al.,2021. *Pressure leaching of wolframite using a sulfuric-phosphoric acid mixture*.J. Minerals Engineering, 169, 106941.

ONGHENA, B., BORRA, C. R., VAN GERVEN, T., BINNEMANS, K., 2017. *Recovery of scandium from sulfation-roasted leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide.* Sep. Purif. Technol. 176, 208–219.

PARHI, P. K., PARK, K. H., NAM, C. W., PARK, J. T., 2015. *Liquid–liquid extraction and separation of total rare earth (RE) metals from polymetallic manganese nodule leaching solution.* J. Rare Earths 33, 207–213.

QIN, S., WEI, C., LI, M, T., ZHOU, X, J., LI, C, X., DENG, Z, G. et al., 2011.*Dissolution kinetics of vanadium trioxide at high pressure in sodium hydroxide–oxygen systems*. J. Hydrometallurgy.

RAMASAMY, D. L., PUHAKKA, V., REPO, E., SILLANPÄÄ, M., 2018. *Selective separation of scandium from iron, aluminium and gold rich wastewater using various amino and non-amino functionalized silica gels – A comparative study.* J. Cleaner Prod. 170, 890–901.

REID, S., TAM, J., YANG, M., AZIMI, G., 2017. *Technospheric mining of rare earth elements from bauxite residue (red mud), Process optimization, kinetic investigation, and microwave pretreatment.* Sci. Rep. 7, 15252.

RIVERA, R. M., ULENAERS, B., OUNOUGHENE, G., BINNEMANS, K., VAN GERVEN, T., 2018. *Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching.* Miner. Eng. 119, 82–92.

RIVERA, R. M., ULENAERS, B., OUNOUGHENE, G., et al., 2019.*Selective rare earth element extraction using high-pressure acid leaching of slags arising from the smelting of bauxite residue*.J. Hydrometallurgy. 184, 162-174.

SHENGFENG, M., 2012. *Study on extraction technology of scandium from the Bayanobo tailings [D]*, Inner Mongolia University.

US Geological Survey, 2019. *Mineral commodity summaries*.

STEPANOV, S.I., P'Ei, K ., BOYARINTSEV, A.V., et al., 2018. *Use of Machining to Increase the Recovery of Scandium from Refractory Silicate Raw Material*.J. Theoretical Foundations of Chemical Engineering, 52(5), 898-902.

XIONG, X. H., WANG, Z. X., WU, F. X., LI, X. H., GUO, H. J., 2013. *Preparation of TiO2 from ilmenite using sulfuric acid decomposition of the titania residue combined with separation of Fe3+ with EDTA during hydrolysis.* Adv. Powder Technol. 24, 60–67.

XIA, Z, M ., TANG, M, T ., YANG, S, H ., et al., 2015. *Materials balance of pilot-scale circulation leaching of low-grade zinc oxide ore to produce cathode zinc*.J. Canadian Metallurgical Quarterly. 54, 439-445,

ZAKHAROV, V. I., MAIOROV, D. V., ALISHKIN, A. R., MATVEEV, V. A., 2011. *Causes of insufficient recovery of zirconium during acidic processing of lovozero eudialyte concentrate*. Russ. J. Non-ferrous Metals 52, 423–428.

ZHANG, J., EDWARDS, C., 2013. *Mineral decomposition and leaching processes for treating rare earth ore concentrates*. Can. Metall. Q. 52, 243–248.

ZHANG, N., LI, H. X., LIU, X. M., 2016. *Recovery of scandium from bauxite residue-red mud, A review.* Rare Met. 35, 887–900.

ZHANG, W., ZHU, Z., CHENG, C. Y., 2011. *A literature review of titanium metallurgical processes.* Hydrometallurgy 108, 177–188.

ZHANG, Y., HUA, Y., GAO, X., XU, C., LI, J., LI, Y., et al., 2016. *Recovery of zinc from a low-grade zinc oxide ore with high silicon by sulfuric acid curing and water leaching.* Hydrometallurgy 166, 16–21.

ZHANG, Y., ZHAO, H., SUN, M., ZHANG, Y., MENG, X., ZHANG, L. et al., 2020. *Scandium extraction from silicates by hydrometallurgical process at normal pressure and temperature.* J. Mater. Res. Technol. 9, 709–717.

ZHANG, G, F ., YAN, P ., YANG, Q, R., 2013. *Experimental Study on Concentrating Scandium by Leaching from Associated Scandium Ore.*J. Advanced Materials Research. 734-737, 1033-1036.

ZHANG, S.H., LI, T., ZHU, B.C., ZHU, Z.B., et al., 2005. *Gas–liquid mass transfer in three-phase mechanical agitated reactor*. J. Chem. Ind. Eng. 56, 200-226.

ZHU, X ., ZHANG, Y ., HUANG, J ., et al., 2012 .*A kinetics study of multi-stage counter-current circulation acid leaching of vanadium from stone coal*.J. International Journal of Mineral Processing. 114–117, 1-6.