Physicochem. Probl. Miner. Process., 61(4), 2025, 208752 | Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp

ISSN 1643-1049

Ultrasound-enhanced ilmenite acid leaching and optimization research

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Abstract: In the production of titanium dioxide pigment via the sulfuric acid process, maintaining a high sulfuric acid concentration (85%) is essential for efficient titanium leaching. However, this conventional approach generates substantial waste acid (20% sulfuric acid). By reducing the reactive sulfuric acid concentration, the waste acid recycling rate can be increased, thereby decreasing waste acid production and conserving fresh sulfuric acid consumption. In this paper, ultrasonic activation is employed to enhance the premixing process of ilmenite. The effects of sulfuric acid concentration, ultrasonic power, and ultrasonic time on the ilmenite leaching rate were studied using an L9 (33) orthogonal test. In order of significance, the primary factors influencing the ilmenite leaching rate are sulfuric acid concentration, ultrasonic power, and ultrasonic time. The optimal conditions for ilmenite leaching are as follows: a sulfuric acid concentration of 80%, an ultrasonic power of 800 W, and an ultrasonic time of 5 min. Under these conditions, the ilmenite leaching rate can reach 93.07%. Ultrasonic cavitation can reduce the size of ilmenite while increasing its surface area and surface reactivity. Furthermore, the ultrasonic strengthening effect can enhance the porosity of the reactive solid phase, promote the diffusion of sulfuric acid on the surface of the ilmenite, and improve the acid hydrolysis rate of ilmenite concentrate at low concentrations.

***Keywords*:** ultrasonic enhancement, ilmenite, acid leaching, orthogonal test, cavitation effect

1. Introduction

Ilmenite is an important source of titanium resources and is widely used in chemical, aviation, military and other industries. The utilization of ilmenite not only contributes to the production of titanium dioxide, titanium alloy and other products, but also effectively uses its associated iron resources, reducing environmental pollution and resource waste. With the global emphasis on environmental protection and sustainable development, the application prospect of ilmenite is broad, especially in aerospace, medical treatment and chemical industry. Liu et al. (2023) studied the effect of fluoride ion on titanium coordination structure. The results showed that fluoride ion could reduce the reduction steps of titanium ion and had a great impact on the valence ratio of titanium ion, which provided a broad application prospect for the continuous process of molten salt electrolysis. Bu et al. (2022) studied the optimization and softening melting behavior of the full particle integrated burden of high chromium vanadium titanium magnetite. The results showed that the segregation of flux and acid pellets in the proportion and alkalinity of high chromium vanadium titanium magnetite was the main reason for the better soft melting performance of the overall burden, which provided a theoretical basis for optimizing the burden structure of blast furnace and strengthening the smelting of high chromium vanadium titanium magnetite. Yu et al. (2025) studied the collector enhanced flotation separation of ilmenite and ilmenite. The results showed that a new HMPA was successfully synthesized and evaluated as an efficient collector. HMPA showed excellent collection ability and selectivity, making it a very promising flotation collector for ilmenite. Therefore, the rational utilization of titanium resources and the development of ilmenite are of great significance to ensure process safety and promote the healthy development of economy.

DOI: 10.37190/ppmp/208752

At present, the main way to develop titanium resources in China is to use sulfuric acid process. The primary steps in the sulfuric acid process involve the acid hydrolysis of ilmenite, the concentration of the titanium solution, hydrolysis, calcination, and surface treatment. The production process comprises multiple steps and lengthy workflows, primarily relying on intermittent operations. This results in significant energy consumption, as well as the generation of substantial amounts of "three wastes" (waste gas, waste water, and solid waste) and by-products, thereby leading to considerable environmental pressure. The sulfuric acid process for producing 1 ton of titanium dioxide requires approximately 3.8 tons of 98% sulfuric acid, resulting in the generation of 6 to 8 tons of waste acid at a concentration of 20%, along with by-products including 2.5 to 3.0 tons of ferrous sulfate (Li et al., 2017). To address the significant issue of waste acid generated during the sulfuric acid process for titanium dioxide production, this study investigates a theoretical and technical approach to low-concentration acid leaching of ilmenite. The objective is to increase the recycling rate of waste acid by 20% (Wang et al., 2019), reduce sulfuric acid consumption by 98%, minimize the costs associated with "three wastes" treatment, and enhance resource utilization efficiency. This research holds substantial scientific significance and presents promising industrial application prospects.

The acid leaching of ilmenite is a process that involves the transformation of titanium elements from the solid phase to the liquid phase (Zhang et al., 2009). This process falls under the category of heterogeneous liquid-solid reactions. Typically, methods such as mechanical activation, ultrasound, and thermal activation are employed to enhance the surface activity of mineral powders. These techniques strengthen the mass transfer processes between leaching agents—commonly acidic solutions—and mineral particles, facilitating the diffusion of leaching agents on the surfaces of solid particles and ultimately improving extraction efficiency (Wan et al., 2024). Mechanical grinding can achieve a finer particle size of the ore, thereby increasing the contact area between the mineral powder and H_2SO_4. Additionally, the mechanical energy generated during grinding may lead to lattice distortion and create lattice defects, which facilitate mineral dissociation and enhance reaction efficiency (Nie at al., 2020). Li et al. (2006) investigated the effect of mechanical activation on the dissolution of ilmenite in dilute sulfuric acid. The results indicated that mechanochemical activation significantly enhanced the leaching rate of titanium from 36% to 76% by reducing particle size and increasing the reaction contact area. Furthermore, the grinding process contributed to lattice distortion and amorphization of the crystals, thereby lowering the activation energy required for leaching. Compared to dry milling, wet milling proved to be more effective; it resulted in a narrower, smaller, and more uniform particle size distribution for ilmenite. The application of wet milling treatment on ilmenite facilitated its leaching reaction with dilute acid (60% H_2SO_4), making both waste acid reuse feasible and economically viable. Khorramshahi et al. (2006) enhanced the leaching rate of copper from chalcopyrite in dilute sulfuric acid through mechanical activation. The results indicate that the improvement in the copper leaching rate can be attributed to several factors: (i) the the formation of lattice defects on the surface of ore particles, (ii) lattice distortion resulting from mechanical activation, and (iii) a decrease in grain size along with the appearance of amorphous chalcopyrite. The combined influence of these factors leads to a significant enhancement in the copper leaching rate. The application of Odebiyi et al. (2022) in the process of mechanical activation extraction metallurgy has greatly improved the ability of waste to transform into wealth. EVM can be effectively recovered from secondary resources by mechanical activation hydrometallurgy process to solve the shortcomings of mechanical assisted leaching. Odebiyi et al. (2024) studied the effect of mechanochemical activation parameters on vanadium recovery from vanadium bearing steel slag. The results showed that the activation process of particle size and the corresponding surface area required by the recovery process were effectively reduced, the leaching temperature was reduced, the lattice deformation was increased, and water-soluble compounds were produced. Wei et al. (2009) investigated the optimization of the leaching process associated with Panxi ilmenite. The results indicate that the grain size of ilmenite decreases from 626 nm to 318 nm after 4 hours of mechanical activation, while the lattice distortion decreases from 0.0158% to 0.0235%. Mechanical activation process can effectively reduce the grain size and generate lattice distortion to promote dissociation, however, the titanium leaching rate remains relatively low, consistently below 80%. The cavitation effect of ultrasonic waves can diminish particle size, distort the crystal lattice, and increase the porosity of ore powder, making it an effective technology for enhancing mineral leaching. Chen et al. (2023) found that ultrasonic treatment facilitates the removal of epoxy resin and fine metal particles from the surface of glass fiber, promotes particle dispersion, and significantly enhances metal recovery. The results indicate that ultrasonic treatment enhances the hydrophobicity of non-metallic components. Consequently, the flotation performance of these non-metal components improves, leading to an increased efficiency in the reverse flotation separation of metal and non-metal components. Balasubrahmanyam Avvaru et al. (2006) The improvement of the ultrasound-induced leaching rate occurs in two steps: (1) the fragmentation of MgF_2 particles increases the specific solid-liquid interface area and the surface diffusion rate of reactive substances; (2) the convective diffusivity of the leaching acid solvent is enhanced as it moves through the micropores of MgF_2, which results from the agglomeration structure formed due to the convective motion generated by the cavitation phenomenon at the solid-liquid interface. The application of ultrasound enhances the overall recovery rate while achieving low concentrations of leaching acid and reducing leaching operation time. Khan et al. (2024) studied the effects of leaching time and temperature on vanadium recovery. Their results indicate that under conditions of 15 vol% sulfuric acid and 3 wt% CaF, the leaching recovery of vanadium can be increased from 87.86% to 92.93%. Furthermore, the presence of ultrasound can elevate the leaching recovery to as high as 87.5%. Dynamics demonstrate that the vanadium leaching process is influenced by both diffusion through product and ash stratification, as well as a reaction constant that is significantly higher in the presence of ultrasound. This enhancement promotes the release of vanadium and accelerates the diffusion rate of shale. Consequently, ultrasonic-assisted leaching may represent a promising technique for improving the leaching efficiency of vanadium from low-grade V-bearing shale. The ultrasonic enhanced mineral leaching process is only applicable to liquid-phase reaction systems. The acidolysis of ilmenite is conducted at elevated concentrations of sulfuric acid and temperature. Once the reaction is initiated, the system rapidly transitions to a solid phase, which restricts the effectiveness of ultrasonic cavitation. Consequently, further research is needed to explore methods for enhancing the acidolysis process of ilmenite using ultrasound.

Currently, much of the research focuses on conventional leaching methods for titanium extraction, while studies on ultrasonic-enhanced pre-mixing processes for titanium are relatively scarce in the published literature. In this work, an ultrasonic-assisted pre-mixing process for ilmenite was employed (Zhai et al., 2020). The ilmenite was subjected to ultrasonic activation with a sulfuric acid pre-mixed slurry before water was added to initiate the reaction. By leveraging the multiple effects of ultrasound, we aimed to disrupt agglomerates and crystal structures of the ilmenite and reduce diffusion layer thickness, thereby facilitating mass transfer between the ilmenite and sulfuric acid and enhancing its leaching efficiency. During the pre-mixing process, ultrasound was utilized to break down larger particles within the ilmenite, exposing encapsulated materials and promoting contact between sulfuric acid and minerals. This approach significantly improved the leaching efficiency of titanium. The study investigated various conditions related to sulfuric acid pre-mixing processes for ilmenites as well as the impact of ultrasound on these processes. Specifically, we examined how factors such as sulfuric acid concentration, ultrasonic power, and duration influenced titanic leaching rates. Optimal leaching conditions were determined through this analysis, along with a detailed examination of mechanisms that enhance both titanic recovery rates and overall extraction efficiencies.

2. Materials and methods

2.1. Experimental materials

PTK10 ilmenite produced by Pangang Group was used in this study. 98% sulfuric acid (Chengdu Cologne Chemicals Co., Ltd., 98%). Aluminum sheet (Chongqing Tiantai Aluminum Co., Ltd., 99.5%). Ferriammonium sulfate standard solution (Panzhihua Iron and Steel Group vanadium and Titanium Resources Co., Ltd., 0.005 mol/l). As shown in Table 1 and Fig. 1, the main phases of ilmenite are $FeTiO_3$ and Fe_2O_3. The median particle size D50 of ilmenite is 0.126 μm. Dry at 120 ℃ for 24h before use.

Table 1 Main chemical composition of ilmenite concentrate/%

Fe_2O_3	FeO	TiO_2	Al_2O_3	CaO	MgO	P_2O_5	SiO_2
6.15	37.95	46.62	0.80	1.20	3.03	0.021	3.23

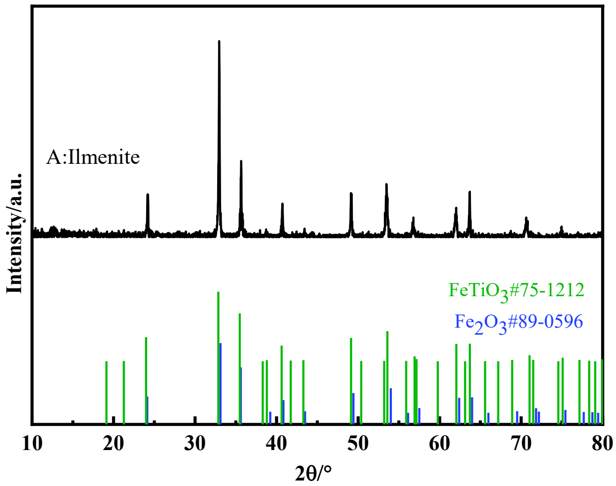

Fig. 1. XRD analysis spectrum of ilmenite

2.2. Experiments

Accurately weigh 100 g of ilmenite into the beaker, and then add 86.51 mL of 98% sulfuric acid to prepare a slurry. The slurry is ultrasonic premixed under the ultrasonic crusher (model: yt-lc-1000 W, input power: 10-1000 W, ultrasonic frequency: 20-25 kHz) for a certain time (Xia et al., 2013), Subsequently, 35.82 mL of deionized water is added to the beaker, which is preheated to 160 °C while stirring at a speed of 250 r/min to initiate the main reaction. The specific acidolysis process flow chart is illustrated in Fig 2. The leached slurry is then filtered and washed with 10% sulfuric acid to prevent the hydrolysis of titanium ions. Finally, the volume of the filtrate is measured as V. The filtrate is dried in a constant temperature oven at 120 °C for 12 hours, and the weight is recorded as m. The content of TiO_2 in the filtrate was determined by chemical titration. In the presence of hydrochloric acid, tetravalent titanium was reduced to trivalent titanium with aluminum sheet, and then titrated with ammonium ferrate sulfate standard solution until trivalent titanium was completely converted to tetravalent titanium. When one drop of standard solution is excessive, the red complex formed by iron ion and indicator thiocyanate is the titration end point, and the leaching rate η is calculated using the following formula (1) (Zheng et al., 2016).

$$\eta = \frac{C_1 \times V}{C_2 \times m + C_1 \times V} \times 100\% \tag{1}$$

In this context, C_1 represents the concentration of TiO_2 in the filtrate, measured in grams per liter (g/L); V denotes the volume of the filtrate in liters (L); C_2 indicates the percentage content of TiO_2 in the filter residue, expressed as a percentage (%); and m refers to the mass of the filter residue, measured in grams (g).

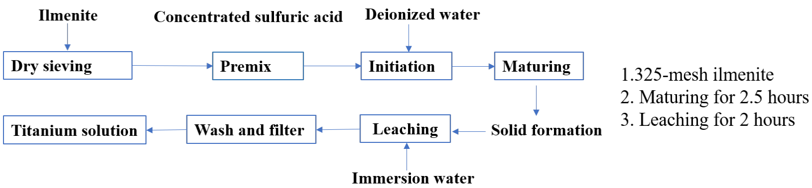

Fig. 2. Schematic diagram of acidolysis process

Note: A stirring speed of 250 r/min is considered the optimal stirring rate for conventional low-concentration acid hydrolysis.

2.3. Experimental design

Referring to existing research and theoretical frameworks, three main factors were selected for the test: sulfuric acid concentration (A), ultrasonic power (B), and ultrasonic time (C). The levels of these three factors were chosen within an appropriate range. Using the leaching rate of titanium dioxide as the performance index, experiments were conducted according to the orthogonal table of L9 (33) (Maazinejad et al., 2020). This approach facilitated the optimization of the process, ultimately leading to the determination of the leaching process conditions for ilmenite. The orthogonal factors and their corresponding levels are presented in Table 2.

Table 2. The level and dosage of each factor in the orthogonal test

level	A Ultrasonic power /W	B Sulfuric acid concentration/%	C Ultrasound time/min
1	600	60	3
2	700	70	5
3	800	80	7

Note: The experimental design involves the leaching of ilmenite using low-concentration acid enhanced by ultrasound. During the pre-mixing process, operating under a power range of 600 W to 800 W is necessary. The duration of ultrasound exposure has minimal impact on leaching efficiency; therefore, an ultrasonic treatment time of 3 to 7 min is selected. Consequently, with three factors at three levels, the design follows an L9 (33) orthogonal array.

2.4. Test characterization means

The phase composition of ilmenite raw material and its acid leaching residue was characterized by X-ray diffraction (XRD, D/max-rb, Rigaku, Japan). In order to further study the properties of the materials, the phase composition and element distribution of the materials were analyzed by scanning electron microscope (SEM, Hitachi, Japan) and energy dispersive spectrometer (EDS). The particle size distribution of ilmenite samples before and after ultrasonic treatment was determined by laser particle size analysis (Mastersizer 2000, Malvern Instruments, UK). In addition, the specific surface area of the samples before and after ultrasonic treatment was evaluated by Brunauer Emmett Teller (BET) surface area measurement (bsd-660s, Quantachrome Instruments, USA).

3. Results and discussion

3.1. Influencing factor experiment

3.1.1. Sulfuric acid concentration

The concentration of sulfuric acid significantly influences the rate of the acid hydrolysis reaction of ilmenite. Higher acid concentrations effectively enhance the acidolysis reaction rate, with acid concentrations ranging from 83% to 85% commonly utilized in industrial applications (Tahooni Bonab et al., 2024). The effect of sulfuric acid concentration on the titanium leaching rate, in the absence of ultrasonic enhancement, is illustrated in Fig. 2. As shown in Fig. 2(a), the titanium leaching rate exhibits a downward trend with increasing sulfuric acid concentration. There are two primary reasons why the concentration of sulfuric acid contributes to the decline in the titanium leaching rate. First, when the concentration of sulfuric acid is low, the ilmenite does not react with it effectively. Consequently, the heat generated is insufficient to initiate the main reaction, leading to a reduced leaching rate. This can be observed from the reaction system temperature in Fig. 2 (b). The reaction temperature of the system decreases as the concentration of the reaction acid increases. Notably, when the concentration of the reactive acid is below 80%, this decrease is particularly significant. Conversely, at higher concentrations of sulfuric acid, the activity increases, leading to a higher concentration of H^+ and SO_4^{2-}. This increase enhances the likelihood of interactions on the surface of the ilmenite powder. Consequently, H^+ and SO_4^{2-} strengthen the dipole interactions on both the mineral and solid surfaces (Li et al., 2021), thereby accelerating the decomposition rate of the ilmenite.

3.1.2. Ultrasonic power

The sulfuric acid concentration is fixed at 80%, and the ultrasonic treatment duration is set to 3 min to

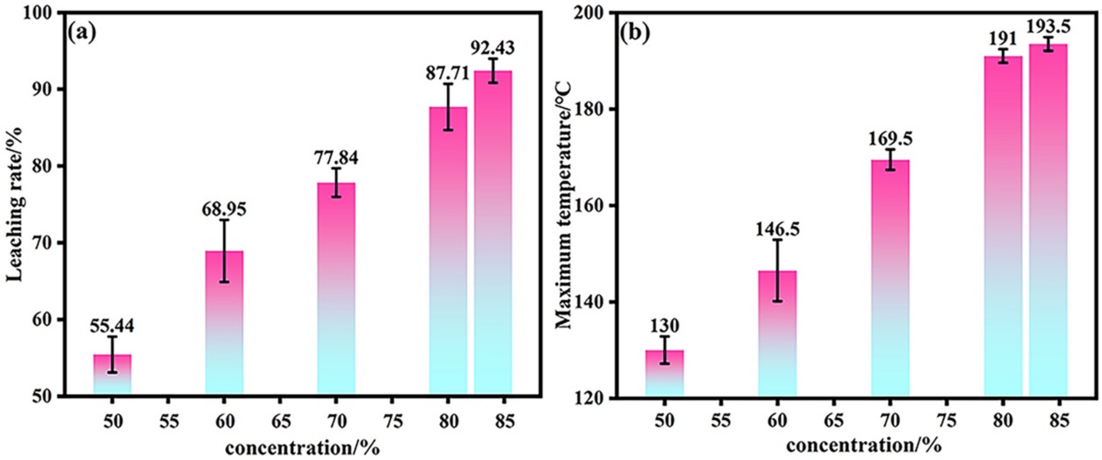

Fig. 2. (a) Effect of sulfuric acid concentration on titanium leaching rate; (b) Effect of sulfuric acid concentration on reaction temperature

investigate the effect of ultrasonic power on the titanium leaching rate. The results are presented in Fig 3. As ultrasonic power increases, the titanium leaching rate initially rises, reaching a maximum of 90.5% when the ultrasonic power reaches 800W. The particle size distribution of ilmenite at various ultrasonic power levels is illustrated in Fig 3(b), while the D10, D50, and D90 values corresponding to these distributions at different ultrasonic powers and durations are presented in Table 3. It is evident that at lower ultrasonic power settings of 600 W and 700 W, the particle size of the ilmenite remains relatively large, with D50 values of 3.102 µm and 3.175 µm, respectively, indicating a wide distribution. When the ultrasonic power exceeds 800 W, the particle size of ilmenite becomes significantly reduced, with a D50 of less than 0.3 µm, resulting in a narrower particle size distribution. The cavitation effect of ultrasound effectively breaks down and refines aggregated ilmenite particles, decreasing the average particle size and narrowing the particle size distribution. This process enhances the surface activity of ilmenite, thereby improving the mixing and mass transfer processes between ilmenite and sulfuric acid, ultimately leading to increased leaching efficiency of titanium (Yag et al., 2021). Due to the high viscosity of the mixed slurry of ilmenite and sulfuric acid, low ultrasonic power is insufficient to induce turbulence within the slurry (Natayana et al., 2008). This inadequacy results in uneven mixing of the ilmenite and sulfuric acid. Consequently, the leaching rate of titanium at 600 W (82.16%) is lower than that achieved through mechanical agitation (87.71%). Furthermore, increased ultrasonic power enhances the leaching of other metal elements (Ran et al., 2024), which adversely affects the leaching of titanium. Furthermore, the cavitation bubble produced by elevated ultrasonic power is excessively large, inhibiting the optimal manifestation of the cavitation effect (Khan et al., 2024). Consequently, the ultrasonic power is set at 800 W. At this power level, the particle size of the ilmenite reaches its minimum value of 0.194 µm, thereby enhancing the titanium leaching rate.

Table 3. Effect of ultrasonic power and ultrasonic time on ilmenite particle size

Ultrasonic power/W	Particle diameter			Ultrasonic times/min	Particle diameter		
	D_{10}/µm	D_{50}/µm	D_{90}/µm		D_{10}/µm	D_{50}/µm	D_{90}/µm
600	1.242	3.102	6.776	0	0.188	0.246	0.303
700	1.021	3.375	9.932	3	0.101	0.184	1.153
800	0.131	0.194	0.250	5	0.029	0.034	0.040
900	0106	0.294	0.422	6	0.127	0.541	0.710
1000	0.201	0.246	0.303	7	0.079	0.169	0.744

3.1.4. Ultrasound time

The sulfuric acid concentration is maintained at 80%, and the ultrasonic power is set at 800 W. The effect of ultrasonic duration on the titanium leaching efficiency is illustrated in Fig 4. As depicted in Fig 4 (a), the titanium leaching rate initially increases with the duration of ultrasound exposure, reaching a maximum of 92.25% at an ultrasonic treatment time of 5 min.

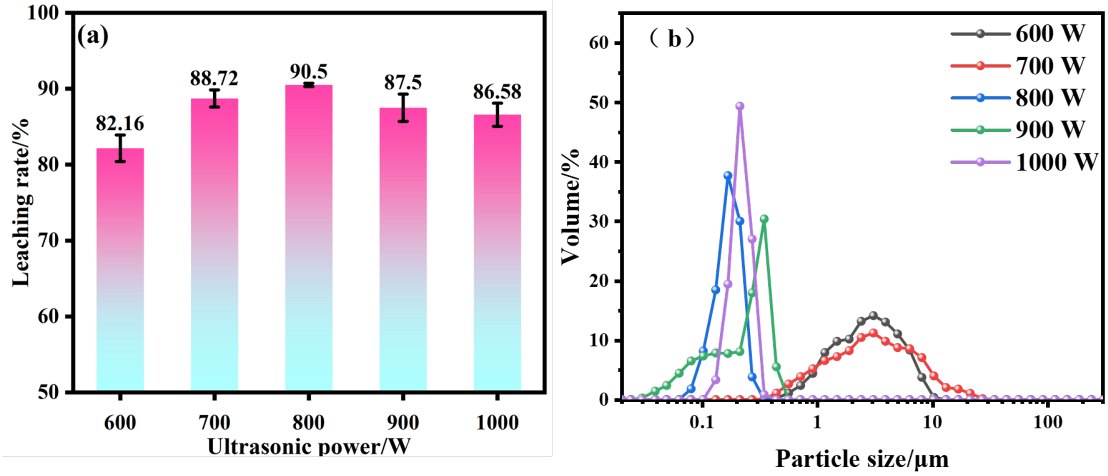

Fig 3. (a) The influence of ultrasonic power on titanium leaching rate; (b) The influence of ultrasonic power on the particle size distribution of ilmenite

The particle size distribution of the ilmenite subjected to varying ultrasound durations is illustrated in Fig 4(b). Additionally, the D10, D50, and D90 values corresponding to the ilmenite's particle size distribution across different ultrasound power levels and exposure times are presented in Table 3. It is evident that at ultrasound durations of 0 min, 3 min, 6 min, and 7 min, the particle size of ilmenite remains comparatively large, with D50 values of 0.246 μm, 0.184 μm, 0.541 μm, and 0.169 μm, respectively. Furthermore, the particle size distribution is broad, exhibiting a double-peak profile in the grain size distribution curve. The observed double-peak distribution indicates that during the specified ultrasonic treatment durations, there is a notable reduction in the population of smaller particles, while a substantial increase in larger particles is evident, leading to further agglomeration of ilmenite particles. Specifically, at an ultrasound exposure time of 5 min, the granulation of the ilmenite is markedly refined, with a D50 value decreasing to below 0.034 μm, resulting in a more uniform particle size distribution. The particle size of ilmenite was reduced from 1.070 μm to 0.015 μm, while the lattice distortion exhibited a decrease from 0.0129% to 0.0326% following ultrasound treatment for durations of 0 min and 5 min, respectively. The ultrasonic treatment of ilmenite enhances its reactivity with sulfuric acid, thereby facilitating the liberation of titanium dioxide from the ilmenite. Under the influence of an ultrasonic field, cavitation bubbles exert a significant erosive effect on the surfaces of solid particles (Shchukin et al., 2011). This process efficiently segregates the insoluble layer present on the particle surface, leading to the ongoing formation of novel reaction interfaces. Consequently, this facilitates a reduction in particle size throughout the leaching process, thereby impacting the leaching rate as a function of particle size (Ruan et al., 2019). The formation of aggregates is frequently observed in ultrasonic processes and is typically attributed to the agglomeration of structurally altered particles following the initial reduction in particle size. Following 5 min of ultrasonic exposure, there is no significant erosion observed on the material's surface, suggesting the generation of numerous transient microbubbles, indicative of the ultrasonic cavitation phenomenon (Sajjadi et al., 2015). If the ultrasonic time is extended again, the slurry temperature will rise and the structure of ilmenite will be destroyed, the particles will agglomerate and the by-product Fe_2SO_4, and the leaching rate of titanium dioxide will not be improved. Therefore, the ultrasonic time is determined as 5min.

The BET specific surface areas of ilmenite samples subjected to ultrasound treatment for durations of 0 min and 5 min are presented in Table 4. Following 0 min of ultrasound exposure, the BET specific surface area of the ilmenite was measured at 0.6325 m^2/g. The specific surface area of the ilmenite sample is measured at 1.1885 m^2/g, which represents an increase of approximately 1.88 times compared to the ilmenite sample subjected to ultrasound for 5 min. Prior studies have indicated that the ultrasonic treatment is a complex process involving both particle fragmentation and agglomeration (Sumitomo et al., 2018). In the preliminary phase of ultrasound treatment, the particles disintegrate rapidly while their agglomeration occurs at a slower rate. Conversely, finer particles tend to agglomerate swiftly over extended durations. This agglomeration process impedes the subsequent fragmentation of smaller particles (Froeschke et al., 2003). Consequently, the specific surface area does not play a critical role in the process.

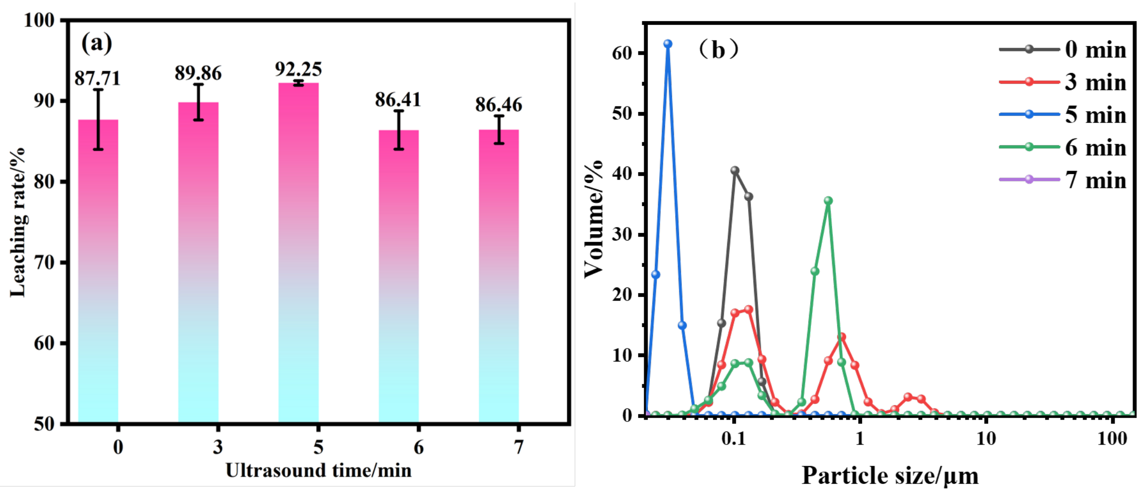

Fig 4. (a) Influence of ultrasonic waves on the leaching rate of titanium; (b) Impact of ultrasonic duration on the particle size distribution of ilmenite

Table 4. Specific surface area of ilmenite before and after ultrasound

Sample	Ultrasonic 0 min ilmenite	Ultrasonic 5 min ilmenite
Specific surface area/m^2/g	0.6325	1.1885

3.2. Orthogonal test results

The range value (R) was the difference between the maximum and minimum values of the average value of K at each level since the orthogonal experiment of three factors, four, three levels, L9 (33) was used in the experiment, and each level of each factor participated in three tests. Table 6 displays the range result.

Table 5. Orthogonal test arrangement and test results

Test number	A	B	C	Titanium leaching rate / %
1	600	60	3	52.7
2	600	70	7	83.66
3	600	80	5	87.79
4	700	60	7	63.02
5	700	70	5	78.93
6	700	80	3	91.74
7	800	60	5	68.72
8	800	70	3	84.69
9	800	80	7	86.46
K_1	74.717	61.48	76.377	
K_2	77.897	82.427	78.48	
K_3	79.957	88.663	77.713	
R	5.24	27.183	2.103	
Optimal scheme	A3	B3	C2	

The range value (R) was the difference between the maximum and minimum values of the average value of K at each level since the orthogonal experiment of three factors, four, three levels, L9 (33) was used in the experiment, and each level of each factor participated in three tests. Table 6 displays the range result.

In conjunction with Table 6, it becomes evident that for the leaching rate of acid leaching titanium, the higher the requisite leaching rate for Ti, the more optimal the outcome. Furthermore, the primary and secondary effects of various factors on the leaching rate of titanium are delineated within the range R. Table 5 and 6 demonstrate that the order of influence of various factors on the titanium leaching rate is as follows: sulphuric acid concentration > ultrasonic power > ultrasonic time. The optimal combination of test conditions is A3B3C2 on a range basis, and the results are presented in Table 7. A variance was made on the data pertaining to the leaching rate of titanium.

Table 6. Range table of influence of various factors on titanium leaching rate

	A (Ultrasonic power) /W	B (Sulfuric acid concentration) /%	C (Ultrasonic time) /min
Average 1	74.717	61.48	76.377
Average 2	77.897	82.427	78.48
Average 3	79.957	88.663	77.713
Range value	5.24	27.183	2.103
Optimal level	800 W	80 %	5 min

Table 7. Variance results of the influence of various factors on titanium leaching rate

Factors	SS	df	F	P	Meaning
Ultrasonic power	223.435	6	0.094	0.912	
Sulfuric acid concentration	27.639	6	22.009	0.002	※
Ultrasonic time	229.271	6	0.015	0.985	
Error	201.632	6			

As can be observed in Table 7, the influence factors on the titanium leaching rate are in the following order of significance: R2 > R1 > R3. The order of significance of the influencing factors on the titanium leaching rate is as follows: B (sulfuric acid concentration) > A (ultrasonic power) > C (ultrasonic time). The concentration of sulfuric acid represents a significant factor affecting the leaching rate of titanium. The second most significant factor is the ultrasonic power, while the ultrasonic time has a negligible effect on the leaching rate. Accordingly, the optimal conditions for leaching ilmenite with sulfuric acid are as follows: an ultrasonic power of 800 W, a sulfuric acid concentration of 80%, and an ultrasonic time of 5 min.

In light of the findings pertaining to the variance, economic cost and operation index, the leaching scheme for titanium from ilmenite is thus determined: the acoustic power is 800 W, the concentration is 80% and the ultrasonic time is 5 min. Validation tests were conducted by the aforementioned conditions, and the results are presented in Table 8.

Table 8. Validation test results

Test serial number	Raw ore quality /%	Filter residue quality /%	Titanium leaching rate /%
1	46.76	6.93	93.07
2	47.83	7.66	92.34
3	47.89	7.95	92.05

As evidenced in Table 8, the titanium leaching rate exceeds 92% in the three verification tests, demonstrating stability in the data. This indicates that the test results are reproducible and reliable under the condition of orthogonal test combination.

3.3. Analysis of the characteristics of filter residue

In order to gain insight into the mechanism of ultrasound-enhanced acidolysis of ilmenite, the crystal structure and morphology of the ultrasound-enhanced filtration residue were characterised using XRD and SEM.

3.3.1. Crystal structure

The X-ray diffraction (XRD) spectra of the ilmenite and acidolysis residue samples are presented in Fig. 5. The characteristic diffraction peaks of acidolysis filter residue and ilmenite are basically the same. The main phase structures are $FeTiO_3$ and Fe_2O_3. The typical peaks are observed at the diffraction angles of (27.44 °, 36.09 °, 41.25 ° and 44.05 °) (He et al., 2025), but the intensity of the diffraction peaks decreases significantly, indicating that the crystal structure of $FeTiO_3$ is destroyed by sulfuric acid after acidolysis. Furthermore, an examination of the XRD spectra of the acidolysis residues at varying ultrasonic activation times (as illustrated in Fig 5) revealed that the ultrasonic activation times exerted varying degrees of influence on the crystal structure of the acidolysis residues. The diffraction peak intensity of the sample subjected to ultrasound for a duration of five min is relatively weak, while the diffraction peak of $FeTiO_3$ is pronounced. This suggests that the crystal strain and grain size are larger during the ultrasound time of five min (Gao et al., 2009). These findings corroborate the hypothesis that the duration of the ultrasound treatment exerts a pronounced influence on the crystal structure and particle size. In comparison to the residues resulting from both ultrasonic and non-ultrasonic filtration, the characteristic peak of TiO_2 in the acid leaching residues was essentially absent, indicating that Ti was largely leached and achieved the desired outcome. The Ti phase observed in the residues following ultrasonic treatment indicates that the application of ultrasonic waves has enhanced the leaching rate of titanium (Rao et al., 2024). As illustrated in Figure 5, the XRD titanium filter slag displays a distinct diffraction peak at 2.000 2θ at 25.685° corresponding to (101) TiO_2.Therefore, the leached residue SiO_2 phase comprises crystalline TiO_2 and amorphous TiO_2 of TiO_2 (Li et al., 2016). The leached residue SiO_2 phase includes both crystalline and amorphous TiO_2; the latter is in the amorphous form of the compound. During the ultrasonic process, the $TiFeO_3$ in solid particles underwent depolymerisation, resulting in an increase in the specific surface area of the ilmenite particles due to the reduction in particle size. As the ultrasonic time increases, the crystallinity of the material in question declines. This suggests that an increase in ultrasound time will result in a reduction in crystal growth (Delgado-López et al., 2013).

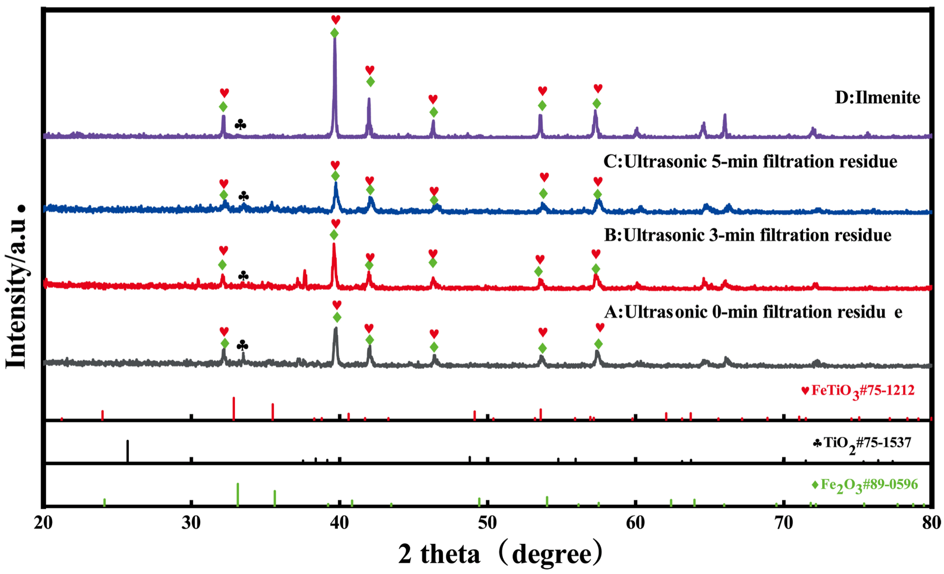

Fig. 5. XRD spectra of filter residue with ultrasonic waves for 0 min, 3 min, and 5 min

3.3.2. Morphology and composition

The scanning electron microscopy (SEM) morphology of the filter residue exceeding 0 min, ultrasound 3 min, and ultrasound 5 min is illustrated in Fig. 6. The surface of the ultrasonic 0 min filter residue is relatively tight and has a block shape. In contrast, the ultrasonic-strengthened filter residue has a convex structure, which is crushed from the block structure of the ultrasonic 0 min residue into numerous fine flake structures following ultrasonic strengthening. The number of coarse particles has slightly changed, and the ore particle size after ultrasound has diminished in general. The alteration of the structure of the refined titanium minerals increases the specific surface area of the filter slag, which becomes fluffier and more porous. The findings suggest that the majority of $FeTiO_3$ crystals detach from the surface of ilmenite particles in the presence of ultrasound, which may facilitate the erosion of ilmenite particles by sulfuric acid. Additionally, the XRD peak intensity of particles is observed to diminish to a certain extent following ultrasound strengthening, thereby corroborating the hypothesis (Liu et al., 2025). Furthermore, the exfoliation effect of ultrasonic cavitation (Li et al., 2018) results in distinct fracture marks at the boundary of the leaching residue. This process facilitates the elimination of the surface film of solid reactants, enhances mass transfer between the solution and solid pores or micropores, and thus reduces internal diffusion resistance (He et al., 2025). The aforementioned differences indicate that ultrasonic energy can impede the growth of solid particles, facilitate the fragmentation of ilmenite particles into smaller particles, promote the renewal of active surfaces, and enhance the solid-liquid reaction, which is of significant importance for the release of titanium from the mineral lattice of ilmenite.

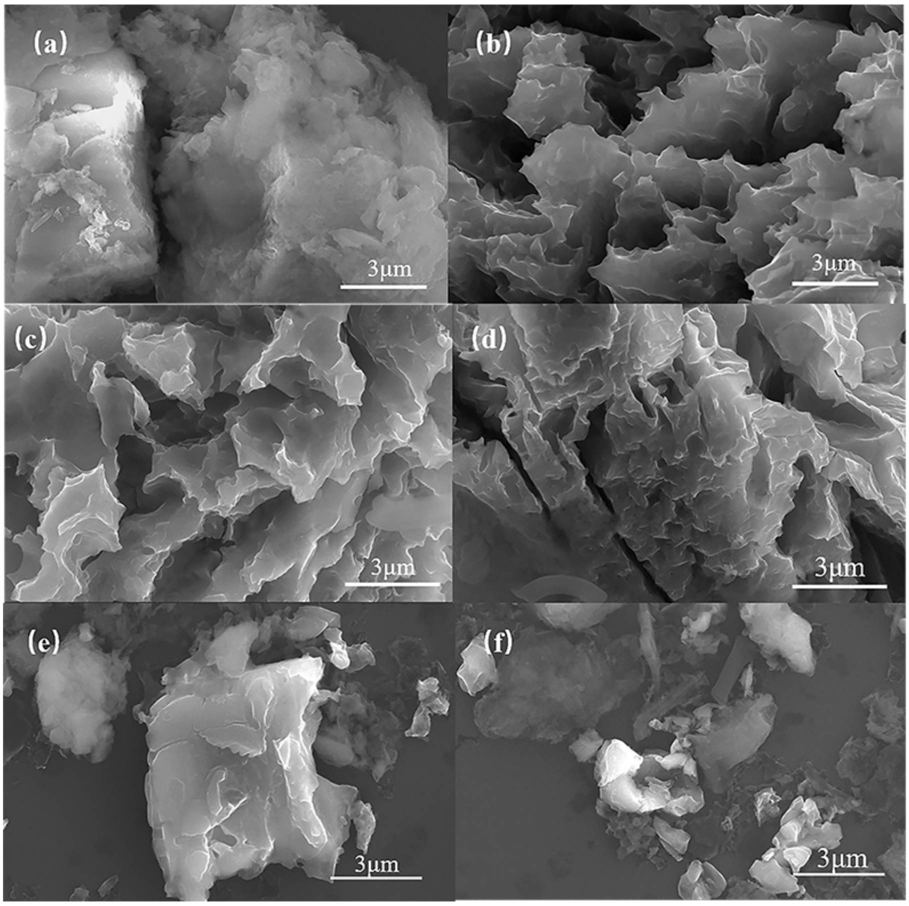

Fig. 6. Scanning electron microscopy morphology of (a, b) ultrasound 0-min filter residue, (c, d) ultrasound 3-min filter residue, and (e, f) ultrasound 5-minute filter residue

As illustrated in the mapping scanning spectrum in Figure 7, the ultrasound 0 min filter residue is composed of 69.7% O, 0.3% Mg, 3.0% Si, 1.0% S, 0.1% Ca, 13.5% Ti, and 12.5% Fe. These findings suggest that the filtration residue contains titanium dioxide, iron oxide, and a minor quantity of silicate. In comparison to the filtration residue, the concentration of titanium dioxide and iron oxide in the latter increases slightly after three min of ultrasound, indicating that the deposition of titanium and iron ions in the ilmenite is promoted after three min of ultrasound. The filtration residue subjected to ultrasound for a period of five min was found to contain 32.8% O, 0.8% Mg, 58.1% Si, 0.4% S, 0.6% Ca, 4.2% Ti and 3.6% Fe. Compared with different ultrasonic times, the content of Ti and Fe decreased, indicating that appropriate ultrasonic time can prevent particle agglomeration and break large solid particles, the opening of solid inclusions, the entry of titanium ions into the liquid phase, and the leaching of titanium in ilmenite (Zhai et al., 2020).

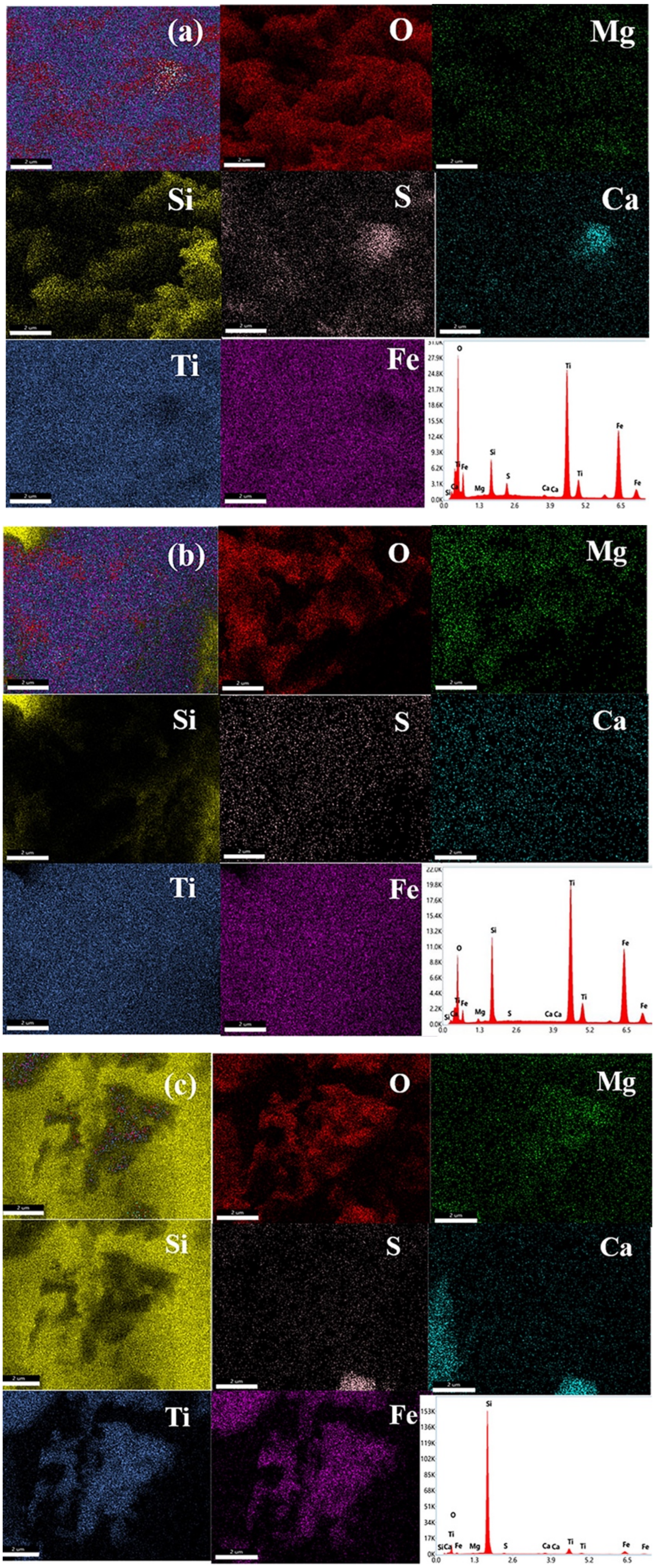

Fig. 7. The following diagrams illustrate the distribution of elements in the samples: (a) ultrasound 0 min filter residue, (b) ultrasound 3 min filter residue, and (c) ultrasound 5 min filter residue

Table 9. Element content of filter residue/%

Element	O	Mg	Si	S	Ca	Ti	Fe
a	69.7	0.3	3.0	1.0	0.1	13.5	12.3
b	52.6	0.7	9.1	0.1	0.07	19.4	18.0
c	32.8	0.6	58.1	0.4	0.6	4.2	3.2

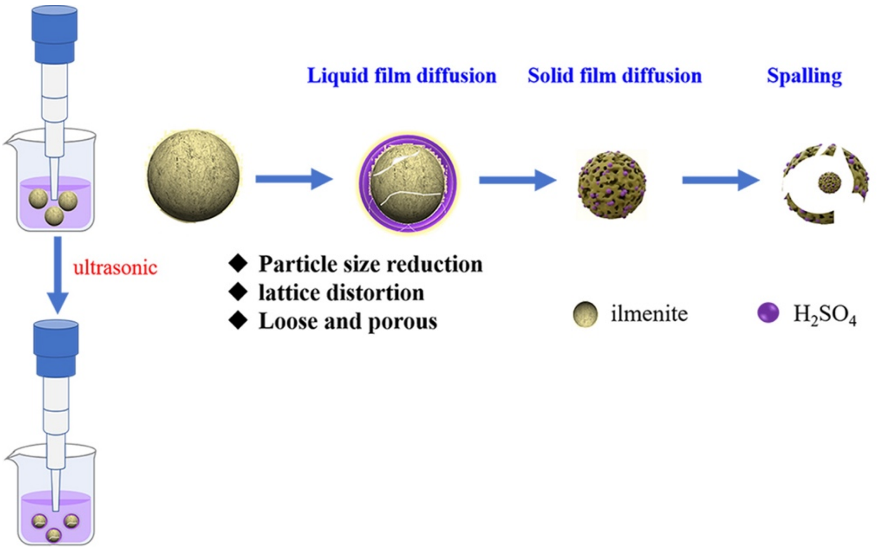

Fig. 8. Schematic diagram of the ultrasonic pretreatment mechanism of ilmenite

The process of decomposing ilmenite with sulfuric acid is a highly intricate one, comprising the following stages: (i) The diffusion of sulfuric acid to the surface of solid particles occurs through the liquid film on the surface of the ilmenite; (ii) A reaction between sulfuric acid and ilmenite occurs at the interface; (iii) The diffusion of sulfuric acid to the unreacted solid core interface occurs through the reaction product (solid phase) on the outer surface of the ilmenite; (iv) The reaction product diffuses to the outer surface of the particle via the liquid film formed by the solid phase; (v) The reaction may occur in either the solid or liquid phase, with the exfoliating particles either adhering to the surface or dissolving into the surrounding medium; The process in question is one of two liquid membrane diffusion, two solid membrane diffusion and a chemical reaction, and it is classified as a membrane diffusion-controlled reaction. The ultrasonic activation of ilmenite was investigated, and it was found that the ultrasonic cavitation effect can facilitate the cleaning of the surface of mineral particles, attenuate the thickness of the boundary layer at the solid-liquid reaction interface, pulverise solid particles, and accelerate the mass transfer rate in solution. Additionally, the particle size and size distribution of ilmenite are conducive to the diffusion of liquid film (Shu etal., 2019). Furthermore, the agglomeration of ilmenite particles promotes the mass transfer process of sulfuric acid on the surface of ilmenite. The asymmetric collapse of ultrasonic cavitation bubbles will result in the generation of a jet under the influence of ultrasonic waves. This, in turn, will lead to a reduction in the thickness of the thermal boundary layer due to the jet flow. The thinner thermal boundary layer will, in turn, facilitate an increase in thermal resistance and flow resistance. It can therefore be concluded that ultrasonic vibration has a positive effect on thermal performance (Zhang et al. 2020). Following ultrasonic treatment, the XRD peak intensity, peak shape passivation and peak area are markedly reduced. Additionally, the grain size of ilmenite undergoes a significant decrease, from 1.070 μm to 0.015 μm. Furthermore, the lattice distortion also exhibits a notable decline, from 0.0129% to 0.0326%. This suggests that ultrasonic enhancement facilitates sulfuric acid in disrupting the crystal structure of ilmenite, thereby damaging its crystal lattice and enhancing the efficiency of the acid hydrolysis reaction. Furthermore, the mechanical effect of the ultrasonic wave also enhances the porosity of the solid phase, resulting in a porous solid phase structure. This not only strengthens the diffusion process of sulfuric acid in the solid membrane but also facilitates the peeling off of the surface product layer

(Cui et al., 2018). The elevated calcium and silicon content in the ilmenite indicates that calcium and silicate materials are being removed, thereby enhancing the leaching rate of titanium.

In accordance with the industrial acid-ore ratio of 1.56:1, the concentration of reactive acid is 84%. The consumption of 98% H_2SO_4 is 3544 kg. In accordance with the industrial acid-ore ratio of 1.56:1, the concentration of reactive acid is 80%. The consumption of 98% H_2SO_4 is 3140 kg. In accordance with the acid-to-ore ratio of 1.56:1, the reactive acid concentration ranges from 84% to 80%. The consumption of 98% fresh sulfuric acid for producing a ton of titanium dioxide was reduced by 404kg.

4. Conclusions

The ultrasonic activation of slurry premixed with ilmenite and concentrated sulfuric acid has been demonstrated to markedly enhance the leaching efficiency of titanium. When the industrial acid-to-ore ratio was set at 1.56:1 and the concentration of reaction sulfuric acid was 80%, the leaching efficiency of conventional leaching of titanium increased from 87.71% to 93.07%. The application of ultrasonic cavitation has been demonstrated to reduce the particle size and particle size distribution of ilmenite concentrate. Furthermore, the specific surface area of the concentrate has been shown to increase by a factor of 1.88 following ultrasound treatment. This process has been observed to inhibit particle agglomeration, thereby enhancing the surface reactivity of the treated ilmenite concentrate. Furthermore, the application of ultrasonic enhancement can enhance the porosity of the reactive solids, which is conducive to the stripping of the reactive solids from the surface of ilmenite particles. Additionally, it facilitates the diffusion of sulfuric acid on the surface of the reactants. Based on the method of ultrasonic activation, the acidolysis reaction of ilmenite can be carried out at low sulfuric acid concentration without reducing the leaching rate of titanium in ilmenite. The concentration of sulfuric acid is to be reduced from the current 84% to 80%. The production of 98% sulfuric acid can be 404 kg per ton of titanium dioxide. The discharge of 20% waste acid represents a more economical and environmentally friendly sulfuric acid process for the production of titanium dioxide pigments.

Note: The data on waste acid is derived from the results of a theoretical calculation.

Acknowledgements

This work was supported by the Scientific Research Foundation of Chongqing University of Technology (No. 0115220003) and the Science and Technology Research Program of Chongqing Municipal Education Commission of China (No. KJQN202201118).

References

1. LIU, S., et al., 2023, *Effect of fluoride ions on coordination structure of titanium in molten NaCl-KCl*. International Journal of Minerals, Metallurgy and Materials, 30(5), 868-876.
2. BU, X., et al., 2022, *Metal extraction from ores and waste materials by ultrasound-assisted leaching -an overview.* Mineral Processing and Extractive Metallurgy Review, 45(1), 28-45.
3. YU, Y., et al., 2025, *Enhanced flotation separation of ilmenite from titanaugite by novel N-hydroxy-3-(4-methoxyphenyl) acrylamide collector*. Applied Surface Science, 163672.
4. LI, X., et al., 2017, *Synthesizing slow-release fertilizers via mechanochemical processing for potentially recycling the waste ferrous sulfate from titanium dioxide production*. Journal of Environmental Management, 186, 120-126.
5. WANG, X., et al., 2019, *Effects of mechanical activation on the digestion of ilmenite in dilute* $H2_SO_4$. Chinese Journal of Chemical Engineering, 27(3), 575-586.
6. ZHANG, Y., T. QI, Y. ZHANG, 2009, *A novel preparation of titanium dioxide from titanium slag*. Hydrometallurgy, 96(1-2), 52-56.
7. WAN, Y., et al., 2024, *Kinetics and mechanism of ultrasonic-enhanced mixed acid leaching of zinc from zinc-bearing dust.* Journal of Environmental Chemical Engineering, 12(5).
8. NIE, W., et al., 2020, *Mechanism and kinetics study of sulfuric acid leaching of titanium from titanium-bearing electric furnace slag*. Journal of Materials Research and Technology, 9(2), 1750-1758.
9. LI, C., et al., 2006, *Effect of mechanical activation on the dissolution of Panzhihua ilmenite*. Minerals Engineering, 19(14), 1430-1438.

10. ACHIMOVIČOVÁ, M., P. BALÁŽ, J. BRIANČIN, 2006, *The influence of mechanical activation of chalcopyrite on the selective leaching of copper by sulphuric acid*. Metalurgija, 45(1), 9-12.
11. ODEBIYI, O.S., et al., 2022, *Sustainability of valuable metals recovery from hazardous industrial solid wastes: The role of mechanical activation*. Journal of Sustainable Metallurgy, 8(4), 1393-1421.
12. ODEBIYI, O.S., et al., 2024, *Effect of mechanochemical activation parameters on vanadium recovery from vanadium-bearing steel slag: Critical speed derivation for wet-ball milling.* Materials Chemistry and Physics, 324, 129697.
13. WEI, L., et al., 2009, *Effects of mechanical activation on the HCl leaching behavior of plagioclase, ilmenite and their mixtures.* Hydrometallurgy, 99(1-2), 39-44.
14. CHEN, L., et al., 2023, *Efficient recovery of valuable metals from waste printed circuit boards via ultrasound-enhanced flotation.* Process Safety and Environmental Protection, 169, 869-878.
15. AVVARU, B., et al., 2006, *Enhancement of the leaching rate of uranium in the presence of ultrasound.* Industrial & engineering chemistry research, 45(22), 7639-7648.
16. KHAN, M.I., et al., 2024, *Enhanced metal recovery using ultrasound-assisted leaching (UAL)*. An overview. Journal of Molecular Liquids, 410.
17. ZHAI, J., et al., 2020, *A review of mineral processing of ilmenite by flotation*. Minerals Engineering, 157.
18. XIA, W., J. YANG, C. LIANG, 2013, *A short review of improvement in flotation of low rank/oxidized coals by pretreatments.* Powder Technology, 237, 1-8.
19. ZHENG, F., et al., 2016, *Kinetics of Hydrochloric Acid Leaching of Titanium from Titanium-Bearing Electric Furnace Slag.* Jom,, 68(5), 1476-1484.
20. MAAZINEJAD, B., et al., 2020, *Taguchi L9 (34) orthogonal array study based on methylene blue removal by single-walled carbon nanotubes-amine: Adsorption optimization using the experimental design method, kinetics, equilibrium and thermodynamics*. Journal of Molecular Liquids, 298.
21. TAHOONI BONAB, S., H. ABDOLLAHI, A. ABBASPOUR, 2024, *The Hydrometallurgical Approach in the Production of a High Content of Titanium Dioxide (TiO_2) from Ilmenite, Direct Hydrochloric and Sulfuric Acid Leaching and Pre-Treatment Methods: A Review.* Mineral Processing and Extractive Metallurgy Review, 1-17.
22. LI, C., ET AL., 2021, *Role of H^+, HF, SO_4^{2-} and kaolin in fixing Hg of coal fire sponge*. Science of The Total Environment, 772.
23. YANG, G., et al., 2021, *Understanding the relationship between particle size and ultrasonic treatment during the synthesis of metal nanoparticles*. Ultrasonics Sonochemistry, 73.
24. NARAYANA, K.L., et al., 2008, *Leaching of Metals from Ores with Ultrasound. Minera*l Processing and Extractive Metallurgy Review, 16(4), 239-259.
25. RAN, J., et al., 2024, *Metal recovery from industrial solid waste by ultrasonic-assisted hydrometallurgical leaching: a review*. Environmental Chemistry Letters, 22(4), 2055-2090.
26. SHCHUKIN, D.G., et al., 2011, *Ultrasonic Cavitation at Solid Surfaces.* Advanced Materials, 223(17), 1922-1934.
27. RUAN, Z., et al., 2019, *Effect of Particle Size Refinement on the Leaching Behavior of Mixed Rare-Earth Concentrate Using Hydrochloric Acid*. ACS Omega, 4(6), 9813-9822.
28. SAJJADI, B., A.A.A. RAMAN, S. IBRAHIM, 2015, *Influence of ultrasound power on acoustic streaming and micro-bubbles formations in a low frequency sono-reactor: Mathematical and 3D computational simulation*. Ultrasonics Sonochemistry, 24, 193-203.
29. SUMITOMO, S., et al., 2018, *Comparison of dispersion behavior of agglomerated particles in liquid between ultrasonic irradiation and mechanical stirring*. Ultrasonics Sonochemistry, 40, 822-831.
30. FROESCHKE, S., et al., 2003, *Impact fragmentation of nanoparticle agglomerates*. Journal of Aerosol Science, 34(3), 275-287.
31. HE, J., et al., 2025, *An effective strategy for coal-series kaolin utilization: Preparation of magnetic adsorbent for Congo red adsorptio*n. Chemical Engineering Science, 304, 120958.
32. GAO, D., et al., 2009, *Effect of ultrasonic power on microstructure and mechanical properties of AZ91 alloy*. Materials Science and Engineering: A, 502(1-2), 2-5.
33. RAO, M., et al., 2024, *Study on ultrasonic assisted intensive leaching of germanium from germanium concentrate using HCl/NaOCl.* Hydrometallurgy, 230.
34. LI, H., et al., 2016, *Hierarchical flower-like nanostructures of anatase TiO_2 nanosheets dominated by {001} facets*. Journal of Alloys and Compounds, 657, 1-7.
35. DELGADO-LÓPEZ, J.M., et al., 2013, *Crystal Size, Morphology, and Growth Mechanism in Bio-Inspired Apatite Nanocrystals.* Advanced Functional Materials, 24(8), 1090-1099.

36. LIU, J., et al., 2025, *Morphology-tunable anhydrous $MgCO_3$ synthesis from magnesite solid waste via salicylic acid-Na2EDTA synergistic leaching and carbonation*. Chemical Engineering Journal, 511, 162168.
37. LI, H., et al., 2018, *Ultrasound augmented leaching of nickel sulfate in sulfuric acid and hydrogen peroxide media.* Ultrasonics Sonochemistry, 40, 1021-1030.
38. HE, J., et al., 2025, *Synthesis of $CuFe_2O_4$/attapulgite composite for removal of methylene blue from aqueous solutions.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 715, 136606.
39. ZHAI, J., et al., 2020, *Recycling of iron and titanium resources from early tailings: From fundamental work to industrial application.* Chemosphere, 242.
40. SHU, K., et al., 2019, *Influence of ultrasound pre-treatment on ilmenite surface chemical properties and collectors' adsorption behaviour*. Ultrasonics Sonochemistry, 57, 98-107.
41. ZHANG, D., et al., 2020, *Investigation on enhanced mechanism of heat transfer assisted by ultrasonic vibration*. International Communications in Heat and Mass Transfer, 115.
42. CUI, J., D. QI, X. WANG, 2018, *Research on the techniques of ultrasound-assisted liquid-phase peeling, thermal oxidation peeling and acid-base chemical peeling for ultra-thin graphite carbon nitride nanosheets.* Ultrasonics Sonochemistry, 48, 181-187.