

## Comparative study on removal of metallurgical silicon impurities by different acid leaching methods

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**Abstract:** Hydrometallurgy is considered a promising method to produce solar-grade silicon (SOG-Si) from metallurgical-grade silicon (MG-Si) due to its advantages of low cost, simple operation, and easy control. In this paper, the effects of particle size of MG-Si, type of acid, leaching time, temperature, and liquid-to-solid ratio on the purification efficiency were investigated in an external field environment with the addition of ultrasound. The purification efficiencies of the two acid-leaching methods were compared. It was found that the simultaneous use of HCl + HNO<sub>3</sub> was more effective than using only HCl for impurity removal in MG-Si: the extraction efficiencies of impurities Fe and Al were increased by 2.2% and 13.4%, respectively. The impurity contents in MG-Si before and after calcination pretreatment were also compared. This paper is expected to help researchers select the appropriate hydrometallurgical technique to reduce the impurity content in MG-Si.

**Keywords:** metallurgical-grade silicon, hydrometallurgy, acid leaching, impurity removal efficiency

### 1. Introduction

With the development of the world economy and industrialization, human demand for energy is increasing day by day (Compaan, 2006). While satisfying their rapid growth, people inevitably must exploit the earth's non-renewable energy in large quantities, leading them into the dilemma of impending resource depletion. Compared with traditional energy sources, solar power generation has the advantages of being environmentally friendly, safe, and convenient, having sufficient resources, etc., which can effectively alleviate the problems of energy shortage and environmental pollution (Sarti & Einhaus, 2002; Swanson, 2004). And advanced silicon technology significantly reduces the cost of solar power generation and improves the efficiency of solar power generation, making the large-scale application of renewable solar energy possible (Yoshikawa et al., 2017). However, the impurities in metallurgical grade silicon (MG-Si) must be reduced to a shallow level to achieve the desired performance for silicon solar cells. Therefore, extremely high demands are also placed on the impurity treatment process for monocrystalline or polycrystalline silicon (Braga et al., 2008).

The huge demand and potential profits have led some electronic-grade polysilicon producers to use their excess production capacity to produce solar-grade polysilicon, even speeding up the deposition rate by 30% based on the modified Siemens process to obtain solar-grade polysilicon. However, the modified Siemens method is challenging to produce solar-grade polysilicon due to its high energy consumption, complex chemical reactions, and severe environmental pollution (Chu et al., 1980). Even increasing the deposition rate will not significantly reduce production costs, so traditional chemical methods to produce solar-grade polysilicon through the modified Siemens method will always be expensive.

Due to the high cost of the Siemens process and environmental pollution, researchers have begun to focus on the hydrometallurgical process to get rid of the current situation of the metallurgical silicon industry today. This process can effectively reduce the content of metal impurities in metallurgical silicon in advance to ensure the subsequent smelting and purification effect, which can increase the purity of MG-Si from 98% to more than 99.9%, with the advantages of simple equipment, low-cost, and

large processing capacity. In general, the leaching process should target as many elements as possible to ensure the economic efficiency of the hydrometallurgical purification method. In addition, the silicon loss must be minimized, and the environmental impact during the treatment process should be minimized. Based on these additional conditions, researchers at home and abroad are investigating hydrometallurgical techniques to achieve silicon purification (Jung et al., 2017). The most common acids used to refine MG-Si in the hydrometallurgical processes include  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HF}$ ,  $\text{CH}_3\text{COOH}$ , and their mixtures (Zhan-Liang et al., 2007).

The purity of metallurgical silicon was 99.9% after continuous acid leaching with  $\text{HCl}$  and  $\text{HF}$  (Santos et al., 1990). Norman et al. obtained 99.9% Si by leaching it in three successive steps with aqua regia, hydrofluoric acid, and hydrochloric acid (Norman et al., 1984). Wang and Yin upgraded crushed MG-Si from 98% to 99.96% through leaching by various acids (Wang et al., 1995; Yin and He, 2002). Although the continuous acid leaching method has excellent effects on treating impurities in metallurgical silicon, it also has some problems, such as consuming more acid and having a long reaction time. Therefore, the mixed acid leaching method appears again in people's vision. There are many kinds of mixed acid leaching, including  $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ,  $\text{HF} + \text{HNO}_3$ , aqua regia ( $\text{HCl} + \text{HNO}_3$ ),  $\text{HNO}_3 + \text{HF} + \text{CH}_3\text{COOH}$ , and  $\text{HCl} + \text{HF} + \text{CH}_3\text{COOH}$ , etc. (Rui et al., 2012). It has been confirmed that aqua regia can chemically crack metallurgical silicon, thereby breaking the silicon or exposing impurities. Using mixed acids or successive steps with various acids in acid leaching will increase the cost and complexity. Sakata (Sakata et al., 2002) studied the effect of the Ca addition on removing Fe and Ti from MG-Si by acid leaching, but the Ca element as an impurity was introduced into the acid leaching. Juneja and Mukherjee (1986) researched that 99.95% pure Si was obtained by leaching 150  $\mu\text{m}$  MG-Si through hydrofluoric acid at 50°C. Therefore, much research tries to improve the impurity removal performance of metallurgical silicon by improving the experimental conditions of hydrometallurgical technology (Ma et al., 2009). The distributions of the metallic elements Al, Fe, Ca, Ti, and Cu were analyzed by an electron probe microanalyzer. The metallic elements segregate at the boundaries and form alloy phases such as Si-Fe, Si-Ca, Si-Fe-Al, Si-Fe-Ti, Si-Fe-Al-Ti, Si-Fe-Al-Ca, and Si-Fe-Al-Ca-Ti. When the cast MG-Si is crushed, breakage occurs mostly at grain boundaries due to their low strength. Thus, if MG-Si lumps are crushed to a particle size equivalent to multi-crystalline grains (the microscopic structure of MG-Si is shown in Fig. 1), a significant portion of the metallic impurities are exposed on the grain surface. Therefore, purifying crushed MG-Si by acid leaching should effectively remove metallic impurities.

Based on previous research results, we proposed a comparative method: first, calcination and quenching of MG-Si, followed by acid leaching in hydrochloric acid ( $\text{HCl}$ ) and a mixture of hydrochloric acid and nitric acid ( $\text{HCl} + \text{HNO}_3$ ), respectively, and applying an ultrasonic field during the acid leaching process to compare the removal efficiency of the two acid leaching methods, which is essential to further reduce the concentration of metal impurities in the acid leaching process of Mg-Si. The concept of MG-Si processing is shown in Fig. 2.

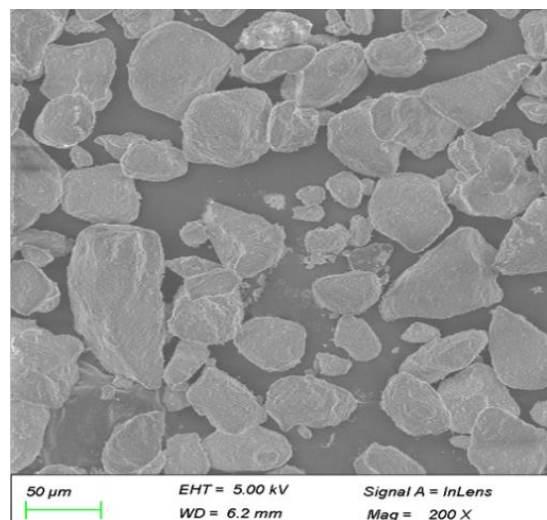


Fig. 1. Microstructure of MG-Si

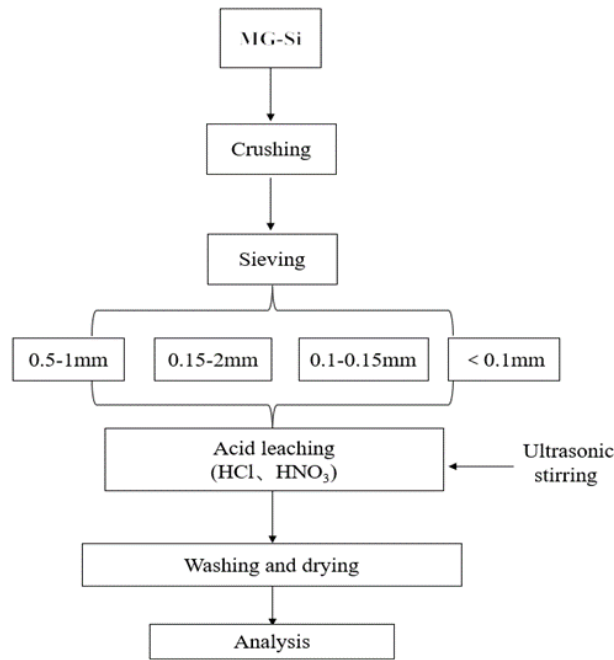


Fig. 2. Concept of MG-Si processing

## 2. Materials and methods

### 2.1. Raw materials

The raw material for MG-Si comes from a power plant in Sichuan. Its purity was about 95.68%. All chemicals used were not subjected to any secondary treatment. The chemical composition of MG-Si was analyzed by X-ray fluorescence (XRF) spectrometry. Scanning electron microscopy was used to observe the microstructure of the silica powders before and after acid leaching. Eq. (1) was used to calculate the removal efficiency of the impurities Fe and Al.

$$\eta = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

where  $\eta$  is the impurities removal efficiency of Fe and Al;  $m_0$  and  $m_1$  are the content of metallurgical silicon impurities (Fe, Al) before and after acid leaching, respectively (Ebrahimfar, 2019).

The concentration difference of impurities in the solid-liquid phase of MG-Si increases with decreasing temperature. This property is commonly characterized by the segregation coefficient ( $k_i$ ), which is defined as Eq. (2).

$$k_i = \frac{c_s}{c_l} \quad (2)$$

$C_s$  and  $C_l$  are the content of impurity I in the silicon solid and liquid phases, respectively. Hopkins and Rohatgi (1986) reported the segregation coefficients (partition coefficients) for most impurities in MG-Si, which are less than 1 in most metals, except for the impurities boron and phosphorus. The segregation coefficient of metal impurities in silicon is relatively low, such as  $8 \times 10^{-6}$  for Fe and  $2 \times 10^{-3}$  for Al. These metallic impurities tend to accumulate on the surface of the grain or in the interstices of the grain boundary during the curing process of silicon. When the silicon particle diameter is equal to or smaller than the grain boundary size, most metal impurities are exposed on the particle's surface and can be removed by an acid reaction.

For non-precious elements, the main chemical reaction formula is as follows: free  $H^+$  in the leaching agent and metal impurity (M) substitution reaction, which results in the formation of soluble metal ions:



### 2.2. Pre-calcination pretreatment

Before the acid leaching experiments, MG-Si was pretreated in a muffle furnace. 30 g of MG-Si was weighed for calcination and leaching experiments for each experiment, washed with deionized water,

dried in a muffle furnace, and calcined at 300°C for 2 h. After calcination, MG-Si was quenched with deionized water and dried in a drying oven. The dried MG-Si was sieved to obtain average particle sizes of 0.5-1 mm, 0.15-0.2 mm, 0.1-0.15 mm, and less than 0.1 mm, respectively, in preparation for the following acid leaching experiments. The elemental contents of MG-Si before and after calcination are shown in Table 1.

Table 1. Impurity content in MG-Si before and after calcination

The impurity element	Before the calcination (%)	After the calcination (%)
K	1.57	1.38
S	1.49	1.01
Fe	0.147	0.241
Al	0.0856	0.0965
Mg	0.185	0.176

### 2.3. Acid leaching process

The leaching experiments were carried out in a closed vessel. Firstly, different concentrations of HCl solution and HCl+HNO<sub>3</sub> solution were prepared and mixed with MG-Si in a certain solid-liquid ratio. The reaction was carried out in a closed vessel with the addition of an external ultrasonic field. After the response, the solids were rinsed with deionized water and dried. The samples were analyzed using fluorescence spectrometry (XRF) and scanning electron microscopy (SEM). The specific experimental conditions are shown in Tables 2 and 3.

Table 2. Leaching with HCl conditions

Factors	HCl concentration (%)	Temperature (°C)	L/S ratio	Time (h)	Average particle size (mm)
Acid concentration	10,15,20,25	70	4:1	6	0.5-1
Temperature	20	50,60,70,80	4:1	6	0.5-1
S/L ratio	20	70	2:1,3:1,4:1,5:1	6	0.5-1
Time	20	70	4:1	2,4,6,8	0.5-1
Average particle	20	70	4:1	6	0.5-1,0.15-0.2,0.1-0.15,<0.1

Table 3. Mixed acid leaching conditions

Factors	Compound acid ratio (HCl:HNO <sub>3</sub> :H <sub>2</sub> O)	Temperature (°C)	L/S ratio	Time (h)	Average particle size (mm)
Compound acid ratio	2:1:8,3:1:6,4:1:5,5:1:4	70	4:1	6	0.5-1
Temperature	3:1:6	50,60,70,80	4:1	6	0.5-1
S/L ratio	3:1:6	70	2:1,3:1,4:1,5:1	6	0.5-1
Time	3:1:6	70	4:1	2,4,6,8	0.5-1
Average particle	3:1:6	70	4:1	6	0.5-1,0.15-0.2,0.1-0.15,<0.1

## 3. Results and discussions

### 3.1. Effect of leaching temperature

Temperature plays a vital role in the acid-leaching process, and usually, an increase in temperature leads to an increase in leaching efficiency and a reduction in reaction time. The efficiency of homogeneous thermochemical reactions increases by 2-4 times for every 10 K increase in reaction temperature, according to the Van 't Hoff equation. Since chemical reactions require activation energy,

the higher the temperature, the faster the reaction efficiency; the higher the temperature, the stronger the Brownian motion of the diffusion mass, and the easier it is to reach the impurities inside the grain gap, thus enhancing the acid leaching removal effect.

Fig. 3 shows the effect of temperature on the removal efficiencies of impurities by both acid-leaching methods. Considering that too high a temperature causes excessive acid loss, the temperature is capped at 80°C.

As shown in Fig. 3(a), for the leaching with HCl, the impurity removal efficiency increased with the increase in temperature. However, the increase was smooth, and when the temperature was increased from 50 to 80 °C, the removal efficiency of Fe and Al increased by 11.4% and 11.6%, respectively. When the temperature increased from 70°C to 80°C, the removal efficiency of Fe and Al increased by 2.8% and 3.1%, respectively. For mixed acid leaching, as shown in Fig. 3(b), the impurity removal efficiency increased after 70°C. The removal efficiencies of Fe and Al increased by 10.6% and 8.1%, respectively. Also, by comparing Fig. 3(a) and (b), it was found that the impurity removal efficiency of MG-Si using HCl+HNO<sub>3</sub> was higher than that of leaching with HCl.

Thus, in summary, the effect of temperature on the efficiency of acid leaching is significant. On the other hand, it shows the importance of temperature in the leaching process. Considering the volatilization loss of the leaching agent and impurity removal effect, the temperature should be controlled at 80°C.

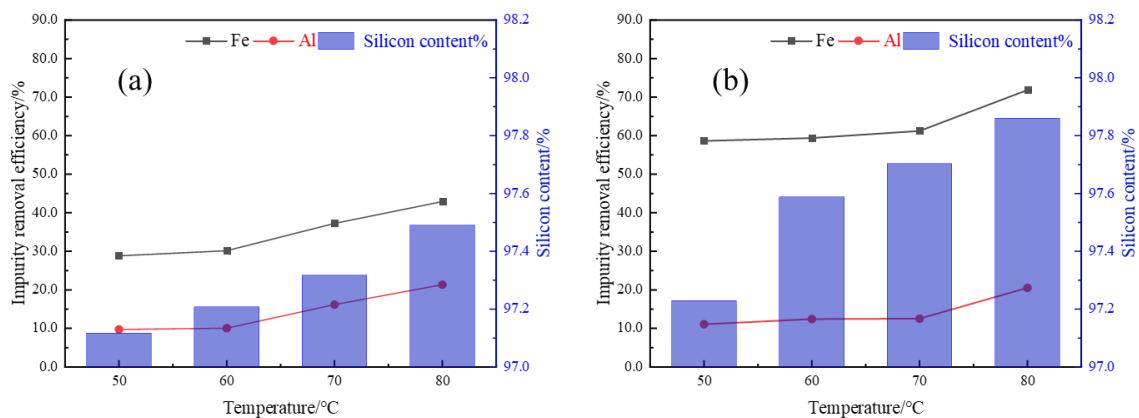


Fig. 3. Effect of temperature on impurity removal efficiency. (a): 20% HCl, 6h, S/L ratio of 1:4, 0.5-1mm; (b):  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=3:1:6$ , 6h, L/S ratio of 4:1, 0.5-1mm

### 3.2. Effect of acid concentration

The variability of the effect of acid concentration on the removal of impurities by the two acid-leaching methods is significant. As shown in Fig. 4(a), the removal efficiencies of metal impurities Fe and Al are maintained at comparable levels throughout the concentration range for leaching with HCl. When the hydrochloric acid concentration exceeds 15%, the difference in the removal efficiencies of metal impurities Fe and Al is greater than 10%. The removal efficiency of mixed acid leaching and leaching with HCl for metal impurities Al is comparable. In contrast, the removal efficiency of mixed acid leaching for metal impurities Fe is much higher than that of leaching with HCl, with the maximum difference reaching more than 15%. From the point of view of molecular collision theory, the greater the concentration of acid, the greater the chance of collision between molecules (ions) and impurities. Therefore, the greater the attention during the reaction, the better the removal of impurities. However, the number of impurities involved in the response in MG-Si is inevitable, and when the concentration of the acid solution reaches a specific value, the chance of collision between molecules (ions) and impurities also tends to saturate; by continuing to increase the concentration of the acid, most of the H<sup>+</sup> in the acid solution cannot come into contact with the impurities. When the acid concentration is too high or too low, it is not conducive to removing impurities from MG-Si. Higher concentrations cause impurities to dissolve as compounds. Still, these compounds tend to saturate in solution and form slightly soluble compounds, making it difficult to increase the removal efficiency further. Therefore, the

concentration of hydrochloric acid in leaching with HCl is controlled at 25%, and  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=4:1:5$  in mixed acid leaching is the most favorable for MG-Si removal.

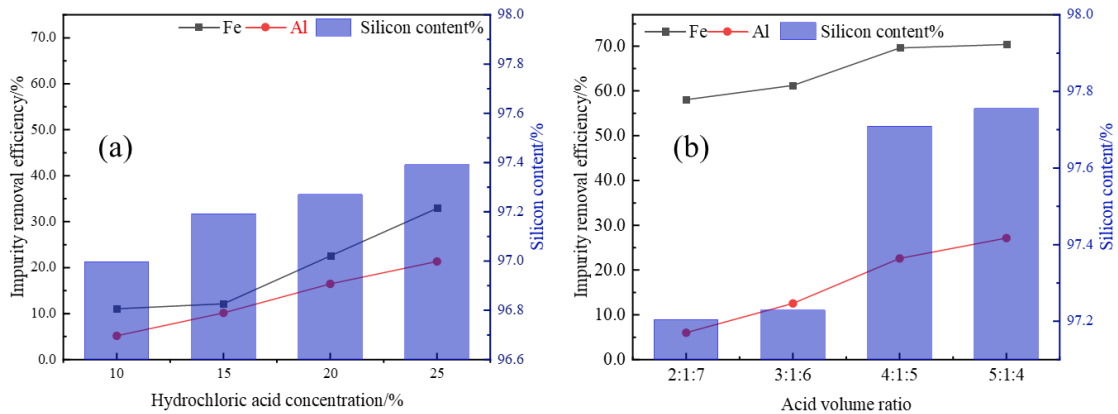


Fig. 4. Effect of Acid concentration on impurity removal efficiency. (a): leaching with HCl; (b): mixed acid leaching (70°C, 6h, L/S ratio of 4:1, 0.5-1mm)

### 3.3. Effect of Liquid-to-solid ratio

The liquid-to-solid ratio is a crucial factor in the MG-Si acid leaching process. A proper liquid-to-solid ratio will promote a complete reaction and avoid acid wastage. The experimental conditions were set to 70°C, 20% HCl, 0.5-1mm, and 70°C, 6h, and  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=3:1:6$ , respectively. The removal efficiency of leaching with HCl increased with the liquid-solid ratio, which was set at a maximum of 5:1 in this study. As shown in Fig. 5. The impurity removal efficiency increased faster in the range of liquid-solid ratios from 2:1 to 4:1, and when the liquid When the solid ratio is 5:1, the removal efficiency of Fe and Al reaches the highest value of 44.3% and 34.8%, respectively. Although the curve continues to rise, the overall trend is not apparent. It can be affirmed that the increase in the liquid-solid ratio is favorable to the reaction during leaching with HCl. Similarly, the impurity removal efficiency in MG-Si increases with the increase of the liquid-solid ratio in mixed acid leaching, but the growth trend is prolonged. Considering the acid leaching process, a high liquid-to-solid ratio will lead to the transition of waste acid into waste solution, which is more difficult to handle and will make it difficult to meet the production requirements in terms of environmental protection and economy. Therefore, the solid-liquid ratio of MG-Si acid leaching and impurity removal is set at 4:1, which is more reasonable.

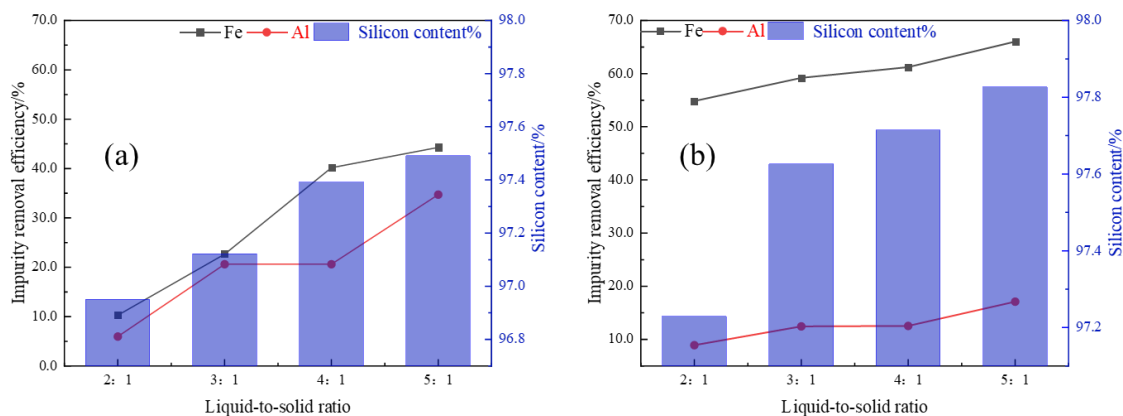


Fig. 5 Effect of liquid-to-solid ratio on impurity removal efficiency. (a): 70°C, 20% HCl, 6h, 0.5-1mm; (b): 70°C, 6h,  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=3:1:6$ , 0.5-1mm

### 3.4. Effect of the particle size

Fig. 6 shows the effect of MG-Si with different particle sizes on the removal efficiency of impurities after leaching in two ways with the experimental conditions: temperature 70°C, 6h, 20% HCl,  $V_{\text{HCl}}:V_{\text{HNO}_3}$ :

$V_{H_2O} = 3:1:6$ , liquid-solid ratio 4:1, and MG-Si particle sizes of 0.5-1mm, 0.15-0.2mm, 0.1-0.15mm, and <0.1mm.

According to the data in Fig. 6, it can be seen that the impurities with particle sizes <0.1 mm are removed best, and the removal efficiencies of Fe and Al for single and mixed acid leaching are 67.9%, 26.5%, and 66.3%, 43.3%, respectively.

The effect of particle size on the removal efficiency of MG-Si showed a tendency to increase with decreasing particle size. The increasing trend of impurity removal efficiency is more significant for mixed acid leaching compared to leaching with hydrochloric acid.

Theoretically, the smaller the particle size of MG-Si in the acid leaching process, the easier the impurities are exposed more on the surface of MG-Si and thus can be easily removed; however, the percentage of MG-Si with tiny particle size is small after crushing and sieving, while the impurity content is high. Therefore, in the subsequent acid leaching and purification process, the selection of particle size should not only be based on the removal efficiency as the only criterion but also on the removal of a small portion of tiny particles of MG-Si can be considered, which can not only avoid the problems of difficult liquid-solid separation and enormous loss of MG-Si during the separation process but also will remove MG-Si with high impurity content and reserve MG-Si with low impurity content. MG-Si, with a particle size of 0.1-0.15 mm, was selected as the experimental raw material to ensure the rigor of the comparison experiment.

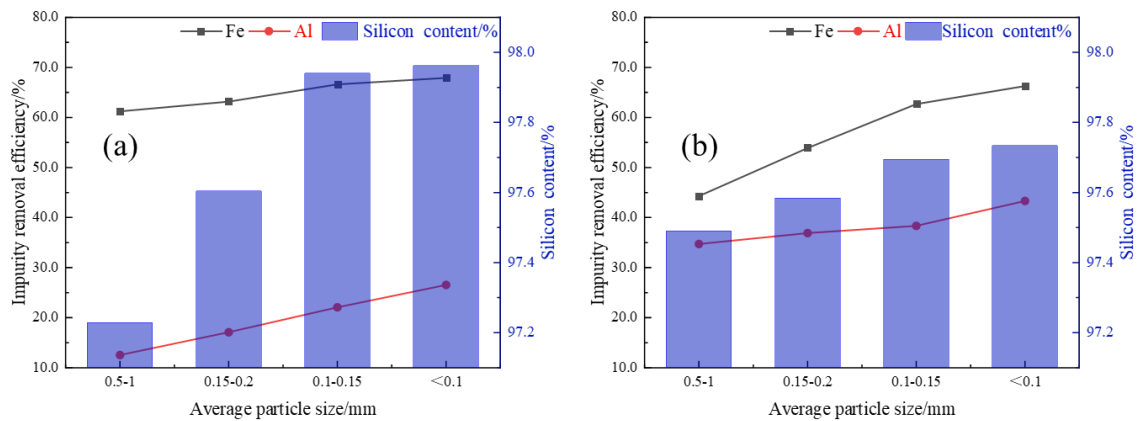


Fig. 6 Effect of particle size on impurity removal efficiency. (a): 70°C, 6h, 20% HCl, L/S ratio of 4:1; (b): 70°C, 6h,  $V_{HCl}:V_{HNO_3}:V_{H_2O} = 3:1:6$ , L/S ratio of 4:1

### 3.5. Effect of time

Fig. 7 shows the effect of time on the removal efficiency of MG-Si impurities under the experimental conditions of a temperature of 70°C, 20% HCl, the liquid-solid ratio of 4:1, time 6h, and  $V_{HCl}:V_{HNO_3}:V_{H_2O} = 3:1:6$ , 0.5-1mm.

The Fe and Al removal efficiencies of single and mixed acid leaching were 62.4%, 23.3%, 69.2%, and 29.5% for 6h, respectively. It can be found that the Al removal efficiency of mixed acid leaching is higher than that of leaching with HCl. The impurity removal efficiency of both acid leaching showed a gradient increase with time, and this increasing trend was significantly weakened after 6h. After 6 h, the removal efficiencies of Fe and Al in leaching with HCl increased by 2.5% and 1.8%, respectively; the removal efficiencies of Fe and Al in mixed acid leaching only increased by 3.3% and 3.6%, respectively. The reason is that the reaction has essentially removed the impurities exposed to the acid in MG-Si. The remaining impurities are in the Si lattice interstices or solid solution, which are difficult to react with. Therefore, the optimal time is 6h.

### 3.6. Characterization of single and mixed acid leaching under optimum conditions

#### 3.6.1. Comparison of leaching efficiencies

According to the above-influencing factors and the results of the experimental analysis and discussion, the reasonable process conditions for the two acid leaching methods were determined as follows:



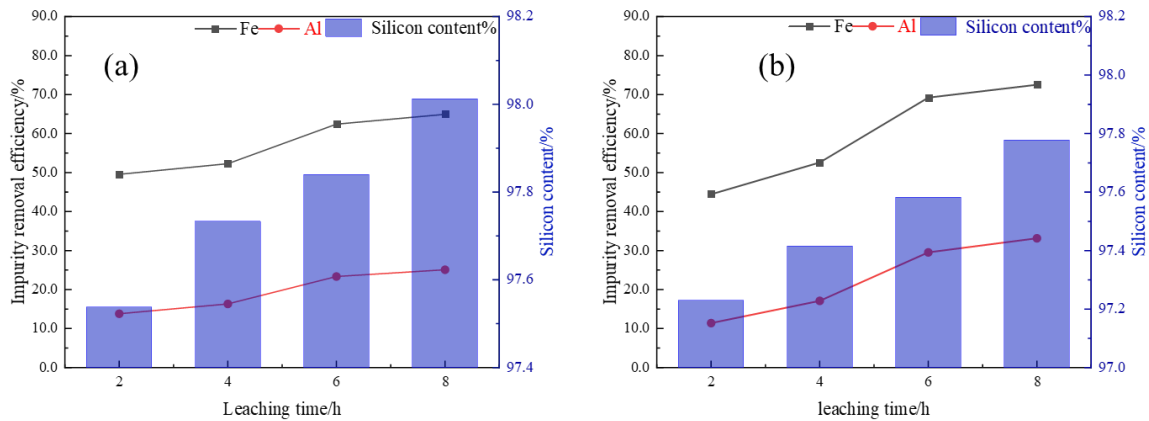


Fig. 7. Effect of time on concentrations of impurity removal efficiency. (a): 70°C, 20% HCl, L/S ratio of 4:1, 0.5-1mm; (b): 70°C,  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}} = 3:1:6$ , L/S ratio of 1:4, 0.5-1mm

Table 4. Comparison of removal efficiencies of impurities from leaching with HCl and mixed acid leaching

Leaching methods	Fe removal efficiency	Al removal efficiency	Silicon content
Leaching with HCl	70.3%	25.2%	97.0%
Mixed acid leaching	72.5%	38.6%	98.8%

leaching with HCl: temperature 70°C, time 6h, MG-Si particle size 0.1-0.15mm, 25% hydrochloric acid, liquid-solid ratio 4:1; mixed leaching: temperature 80°C, time 6h, MG-Si particle size 0.1-0.15mm,  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=4:1:5$ , liquid-solid ratio 4:1. Leaching experiments were conducted under these process conditions, and the impurity removal efficiency and silicon content after acid leaching are shown in Table 4. As can be seen from Table 4, the Fe removal efficiency was comparable between leaching with HCl and mixed acid leaching. Still, the Al removal efficiency of mixed acid leaching was much greater than that of leaching with HCl.

The reason for this analysis may be that by mixing hydrochloric acid with  $\text{HNO}_3$  relative to the pure hydrochloric acid system, the leaching of Fe and Al is promoted by the synergistic effect of the mixed acid due to the strongly oxidizing properties of  $\text{HNO}_3$ . Moreover, according to the study, the  $\text{FeSi}_2$  phase is insoluble in hydrochloric acid solution, and the Si-Fe-Ti phase was not sensitive to HCl. Therefore, the hydrochloric acid solution has poor performance in removing Fe impurities. Under the synergistic effect of  $\text{HCl}+\text{HNO}_3$ , it has a chemical cleavage effect on MG-Si, which can expose the impurities covered by a  $\text{SiO}_2$  film on the surface of MG-Si, thus removing the impurities (Margarido et al., 1994).

### 3.6.2. Morphological analysis

Representative samples processed under two acid-leaching methods were prepared and examined using SEM. Fig. 13 shows the microscopic morphology of pristine MG-Si, leaching with HCl, and mixed acid leaching treated MG-Si. Smooth microspheres and a small number of impurities adhering to the microspheres can be seen in the pristine MG-Si sample (Fig. 13a). After treating MG-Si with HCl, the surface of the microspheres became rough and collapsed, and the main components were severely eroded (Fig. 13 b, c). Although the MG-Si was also eroded after mixed acid immersion, the degree of erosion was less severe, and the MG-Si particles were significantly reduced (Fig. 13d, e). The reaction of  $\text{H}^+$  with MG-Si produces tiny pores, consistent with previous observations, and proves that the acid concentration should be manageable. When the cast MG-Si is pulverized, breakage occurs mainly at the grain boundaries thus if MG-Si is ground to a particle size equivalent to the size of the polycrystalline grains, a significant portion of the metallic impurities presented on the surface of the grains is exposed, which enhances the reaction of the acid solution with impurities.

## 4. Conclusion

Acid leaching of MG-Si is simple and easy to control to remove metal impurities.  $\text{HCl}+\text{HNO}_3$  leaching increased the extraction efficiencies of the impurities Fe and Al by 2.2% and 13.4%, respectively, and the silicon content by 1.8% compared to leaching with HCl. Thus, the acid leaching process parameters were



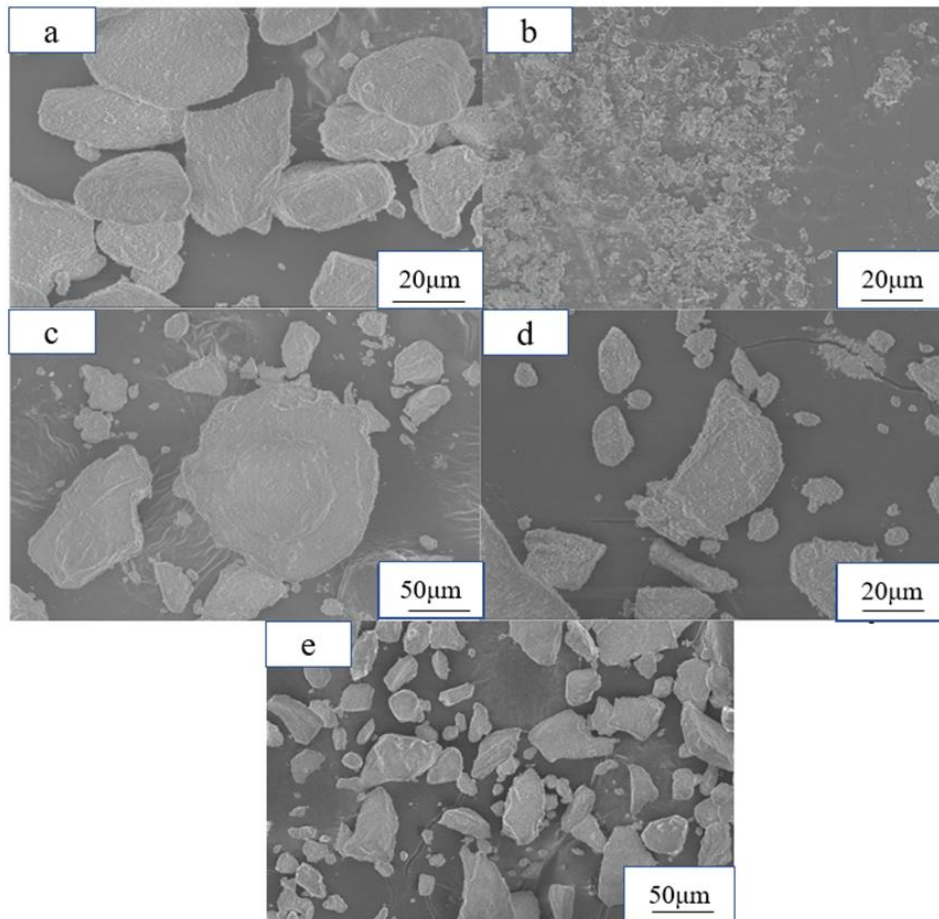


Fig. 8. SEM images under different acid-leaching conditions

optimized leaching temperature of 80°C, leaching time of 6h, MG-Si particle size of 0.1-0.15 mm,  $V_{\text{HCl}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}}=4:1:5$ , the liquid-solid ratio of 4:1, and ultrasonic stirring.

The experimental results showed that the removal efficiency of Fe and Al from MG-Si by mixed acid leaching was higher than that of leaching with HCl. Further studies are needed to assess the viability and economy of the HCl and HNO<sub>3</sub> recycling process.

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