ADVANCED PURIFICATION OF INDUSTRIAL QUARTZ USING CALCINATION PRETREATMENT COMBINED WITH ULTRASOUND-ASSISTED LEACHING

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ABSTRACT

Purification of quartz using an environment-friendly method is important in the contaminants removal. This paper presents advanced method based on calcination pretreatment combined with ultrasound-assisted leaching, for removing iron impurities from industrial quartz. The solvent used is a mixture comprised by diluted hydrochloric acid and oxalic acid. The effects of experimental parameters were investigated and the purification mechanism was discussed using particle size analyzer, scanning electron microscope and polarized light microscope. SiO₂ content of concentrate could be increased from 99.6828 % to 99.9047 %, which achieved 3N level high purity quartz, and Fe₂O₃ content reduced from 0.0857 % to 0.0223 %, under the optimal conditions, i.e., calcination temperature of 900 °C, holding time of 2 h, oxalic acid concentration of 10 g/L, hydrochloric acid concentration of 5%, liquid solid ratio of 5, leaching temperature of 60 °C, ultrasound power of 400 W and treatment time of 30 min. Compared to conventional method, the proposed method significantly accelerates the leaching process and increases the iron removal rate. At the same time, the method also can remove gas-liquid inclusions.

1. INTRODUCTION

High grade quartz is an important non-metallic high-tech raw material, which is widely used in microelectronics, large scale integrated circuits, optical fibers, solar cells, electro-magnetic materials, aerospace, military and other industry sectors (Tuncuk and Akcil, 2016). Currently, whether at home or abroad natural crystal stones are used as raw materials, which after extensive purification allow obtaining high purity quartz products. However, the natural crystal stones are every time more scarce and by this, they turn to be more expensive. Therefore, seeking low price, high efficiency, environment-friendly quartz purification technologies plays a strategic role in this matter. Among all impurities present in quartz, iron is the most difficult to remove. A presence of iron compounds leads to an unacceptable coloring of the final product (Zhang et al., 2012). Iron impurities embedded in the quartz particle or attached to the quartz surface, or wrapped in the gas-liquid inclusion are difficult to be removed. Nowadays, two main chemical acid leaching iron removing methods exist. The conventional leaching method involves the use of hydrofluoric acid mixed in different concentrations with strong mineral acid (i.e. HCl, H₂SO₄, HNO₃) (Tuncuk and Akcil, 2014). For example, Santos et al. (2015) demonstrated the use of dilute HCl + HF to treat quartz lumps. A commercial purity quartz powder obtained contained Fe, Al impurities with concentration below 15 ppm and 50 ppm, respectively. One of the biggest advantages of this method is a high leaching efficiency. However, since silica is soluble in HF, some losses of product are inevitable. Additionally, HF is one of such chemicals which are harmful either to the environment or to the process operator. Because of these limitations, more environment-friendly HF-free methods characterized by loss-free of the target product and less acidic lixivium have been developed. One of the major limitations of these new methods is a processing time, which is prolonged and that they show a low and still unsatisfactory efficiency of iron removal. Therefore, harmless and highly efficient acid leaching processes are required. The research performed in recent years depicted a new trend in this matter. It is characterized by the use of weak organic acids (such as oxalic acid, citric acid, ascorbic acid) as substitute of mineral acid in contaminant treatments (Li et al., 2010; Lee et al., 2007; Li et al., 2016). The application of oxalic acid caused wide attention (Salmimies et al., 2012). For example, Vegliò et al. (1999) showed that 20-30 % of iron was removed when 3 g/L oxalic acid at 80 °C was used. In this case the average size of the quartz sand was 71 μm. Huang et al. (2013) registered an iron removal rate of 37.5 % by oxalic acid, at the optimal concentration of 6 g/L. Taxiarhou et al. (1997) obtained a 40 % of iron removal rate with the oxalic acid concentration of
filtrate was drained and the residue was taken out. The residue was washed in deionized water up to neutral pH. Then it was filtered onto filter paper and dried for subsequent composition analysis.

2.2.3. ULTRASOUND-ASSISTED ACID LEACHING EXPERIMENTS

The ultrasound-assisted experiments were conducted according to the same procedure as described above. The only difference was that an ultrasound probe was immersed into the liquid to be extracted in the glass extraction vessel. Different input powers and treatment times were examined. After the desired extraction time, the same washing procedure was implemented as presented in Section 2.2.2.

All experiments were carried out at least in duplicate and the mean values were taken as the final results. A schematic diagram of the experimental setup is shown in Figure 1.

2.3. EVALUATION AND CHARACTERIZATION

The iron content of the quartz sands was examined by ICP-OES (Varian 715-ES, USA). The iron removal rate was calculated using the following equation:

$$\eta = \left(1 - \frac{\theta}{\alpha}\right) \times 100\%$$

Where $\eta$ is the iron removal rate, $\theta$ is the amount of iron in leached solid samples, $\alpha$ is the amount of iron in ore samples.

The particle size and size distribution of the samples were determined by laser light scattering method (Mastersizer, 2000, Malvern, UK). The morphologies of samples were observed using scanning electron microscopy (ZEISS EVO 18 Special Edition, Germany Carl Zeiss Jena) and polarized light microscope (OLYMPUSB×51TF, Japan).

3. RESULTS AND DISCUSSION

3.1. EFFECT OF MIXED ACID CONCENTRATION ON IRON REMOVAL EFFICIENCY

The influence of oxalic acid (OA) and hydrochloric acid (HCl) concentrations on iron removal in solutions containing liquid solid ratio (L/S) of 5, reaction temperature of 60 °C and leaching time of 8 h were studied. The results are shown in Figure 2. According to this figure, an increase in the OA concentration affects positively the iron removal rate. This can be attributed to the fact that OA reacts with Fe, thus high OA concentration should favor Fe removal.

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>99.5828</td>
<td>0.1158</td>
<td>0.0857</td>
<td>0.0422</td>
<td>0.0387</td>
<td>0.0355</td>
<td>0.0327</td>
</tr>
</tbody>
</table>

*The oxides of less than 0.03 % are not shown.*
removal. However, when the OA concentration exceeds a certain critical value, further increase in OA concentration does not contribute to the enhancement in iron removal rate that it visible in Figure 2 as plateau or even as a decay. The maximum iron removal rate varies depending on the HCl concentration. As it can be observed, 1% HCl shows the lowest Fe removal efficiency. For higher HCl concentrations, the Fe removal depends on the synergistic effect of HCl and OA. An increase in HCl concentration enhances the Fe removal, especially observable at low OA concentrations. When the OA concentration is higher than 4 g/L, iron removal rate at 15% HCl is lower than that for 10% HCl, whereas for concentrations above 8 g/L of OA, the highest Fe removal is observed for 5% HCl followed by 10 and 15%. This trend can be attributed to the fact that in the aqueous system OA reacts according to the following ionization reaction (Parias et al., 1996):

$$\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{C}_2\text{O}_4 = 2\text{Fe} (\text{C}_2\text{O}_4)_3^{3-} + 6\text{H}^+ + 3\text{H}_2\text{O}$$ (2)

$$2\text{Fe} (\text{C}_2\text{O}_4)_3^{3-} + 6\text{H}^+ + 4\text{H}_2\text{O} = 2\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} + 3\text{H}_2\text{C}_2\text{O}_4 + 2\text{CO}_2$$ (3)

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} = 2\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} + 2\text{CO}_2$$ (4)

$$\text{H}_2\text{C}_2\text{O}_4 = \text{H}^+ + \text{HC}_2\text{O}_4^-$$ (5)

$$\text{HC}_2\text{O}_4^- = \text{H}^+ + \text{C}_2\text{O}_4^{2-}$$ (6)

When OA is in mixture with HCl, for low HCl concentration OA is mainly present in HC\(_2\)O\(_4\)\(^-\) form. Hence dissociated OA has higher ability to complex iron ion and consequently promotes its removal. However, when HCl concentration is high, the H\(^+\) in the solution will suppress OA dissociation, OA is mainly present in the molecular form, which is not effective in iron complex reaction. When the HCl concentration is 10% and 15%, a solution contains a high H\(^+\) content that inhibits OA dissociation and hampers the iron removal even for high OA concentrations. For the HCl concentration between 1% and 5%, H\(^+\) in the solution is low and at these concentrations, an additional amount of OA promotes its dissociation and complexation of Fe\(^{3+}\) that improves the leaching efficiency. This effect is observed until the OA concentration reaches 10 g/L. Above 10 g/L of OA, OA inhibits its own dissociation. As it was stated above, in the entire range of the OA concentrations studied, the iron removal rate at 1% HCl is lower than at 5% HCl. The reason for this might be that 1% HCl concentration is too low to promote OA dissociation and the complexity of iron impurities is insufficient. Thus it is difficult to achieve a sufficient dissolution of iron impurities and subsequent removal. Considering all abovementioned aspects, 5% HCl and 10 g/L OA were selected as the optimal concentrations with the iron removal rate of 53%.

3.2. EFFECT OF EXTRACTION TIME ON IRON REMOVAL EFFICIENCY

The influence of extraction time on the iron removal efficiency is presented in Figure 3. A careful analysis of this figure allows stating that longer time promotes iron removal gradually until a certain level is achieved. Above this level there is no further
enrichment in iron removal. It can be concluded that longer time allows more extensive dissolution of iron impurities, making them available for complexing and removal. Once the iron dissolution equilibrium is obtained, no further increase in dissolution of iron, the maximum removal rate can be obtained. At this condition, the extraction temperature higher has a positive effect on iron removal. From the leaching dynamics point of view, the extraction temperature plays an important role in the chemical reaction rate of the leaching process. An increase in extraction temperature makes that the energy of the mineral particles rises, thus the leaching rate accelerates and consequently the dissolution of iron is advanced and balanced quickly. For example, time needed to reach equilibrium was shortened by 2 hours from 8 h at 50 °C to 6 h at 70 °C. However, after reaching equilibrium, an increase in temperature does not improve the iron removal efficiency. For example, when the process was carried out for 8 h, the iron removal rate at 80 °C was lower than that at 60 °C. The reason for this might be that at higher temperature HCl undergoes more extended evaporation and the actual acid concentration decreases contributing to lower dissolution of iron impurities. Therefore, seeking leaching efficiency and taking into consideration the energy requirements, 60 °C and 8 h were considered as the best conditions at which the iron removal rate reached 53 %.

3.3. EFFECT OF LIQUID SOLID RATIO ON IRON REMOVAL EFFICIENCY

The effect of liquid solid ratio on the iron removal was investigated in the range of L/S of 3-8 and the results are shown in Figure 4. The iron removal rate increases with increasing L/S until it reaches 6, then slightly decreases with further increase in L/S. In each experiment performed with the same quality of quartz sands, the increase in the L/S contributes to the increase in the amount of acid solution. Consequently, this improves the fluidity of the slurry. Hence, the mass transfer limitations were avoided contributing to the reaction rate improvements. With an increase in L/S the viscosity of the slurry is lower and the diffusion rate becomes larger. This contributes to higher leaching rate. However, an increase in the L/S not only makes the waste more acidic, but also increases the volume of the leaching mixture. This means an additional capital expenditure, which is a negative effect. An increase in L/S from 5 to 6 improves the iron removal rate from 54 % to 55 %, only increased by 1 %. Therefore, from the economic point of view, the L/S of 5 is more suitable choice.

3.4. EFFECT OF ULTRASOUND TREATMENT ON IRON REMOVAL EFFICIENCY

The influence of ultrasound input power on the iron removal was performed with 100, 200, 300, 400 and 500 W. The iron removal rate increases along the increase in the ultrasound power as shown in Figure 5. However, this increase is visible up to 400 W and further rise of ultrasound power above that one does not improve the iron removal rate that is 64 %. When ultrasound waves pass through the liquid, alternating tensile stress will be put on liquid particles, generating cavitation bubbles that will collapse during the compression process of the liquid. The collapse will cause huge pressure change that leads to severe local temperature rise and associated energy release. Under the impact of the generated local high temperature and strong micro-jet, the impurities attached and embedded on the surfaces of quartz particles will fall off into the mixed acid solution, resulting in many micro-pits on the surface (Du et al., 2010). The pit become deeper and larger, so the mixed acid solution can penetrate easier into the quartz particles, improving the iron impurities removal by a formation.
ADVANCED PURIFICATION OF INDUSTRIAL QUARTZ USING CALCINATION PRETREATMENT

The observed behavior may be attributed to the crystal transformation. Quartz undergoes crystalline transition at 573 °C and 870 °C and both alters the volume of quartz. At 573 °C α-quartz form undergoes structural change to β-quartz with associated 5% volume expansion, whereas at 870 °C β-quartz form changes to β-squamous quartz with a 12% volume expansion (Balitsky et al., 1996; Moore, 1993). Due to a difference of the expansion rate between impurity and quartz, the rapid change in temperature can cause a large number of cracks at the junction of impurity and quartz matrix. Thus impurities embedded in the quartz become exposed and react with acid and the iron removal efficiency can be enhanced. High temperature is beneficial to the increase of the thermal stress during quenching process. At the same time, the increase in the thermal stress facilitates the acceleration of cracks in quartz and impurity. The internal iron impurities are exposed to acid solution and the iron removal rate are increased. However, as it can be seen in Figures 3 and 6, the iron removal rate is much higher at ultrasound treatment than conventional leaching. It increases from 53 % of 8 h for conventional leaching to 64 % of 30 min for ultrasound treatment. A possible explanation for the phenomenon is that the cavitation effect produced by sonication improves the kinetic conditions of the reaction. Ultrasound treatment makes the quartz particles smaller, increases the liquid solid interface and improves the surface diffusion rate of reactants. Thus, it speeds up the iron removal. However, the iron removal rate is almost no increased after 30 min; consequently a 30 min was selected as the optimal treatment time.

3.5. EFFECT OF CALCINATION PRETREATMENT ON IRON REMOVAL EFFICIENCY

The influence of calcination temperature on the iron removal was studied in the temperature range of 500-1000 °C with holding time 2 h. The results are shown in Figure 7. According to Figure 7, the iron removal rate increases from 65 % at 500 °C to 75 % at 1000 °C. The observed behavior may be attributed to the crystal transformation. Quartz undergoes crystalline transition at 573 °C and 870 °C and both alters the volume of quartz. At 573 °C α-quartz form undergoes structural change to β-quartz with associated 5% volume expansion, whereas at 870 °C β-quartz form changes to β-squamous quartz with a 12% volume expansion (Balitsky et al., 1996; Moore, 1993). Due to a difference of the expansion rate between impurity and quartz, the rapid change in temperature can cause a large number of cracks at the junction of impurity and quartz matrix. Thus impurities embedded in the quartz become exposed and react with acid and the iron removal efficiency can be enhanced. High temperature is beneficial to the increase of the thermal stress during quenching process. At the same time, the increase in the thermal stress facilitates the acceleration of cracks in quartz and impurity. The internal iron impurities are exposed to acid solution and the iron removal rate are increased. However, as it can be seen in Figure 7, above the crystal transition temperature, a further increase in calcination temperature does not affect significantly the iron removal rate (74 % at 900 °C and 75 % at 1000 °C), thus considering the energy consumption, 900 °C is more adequate than a 1000 °C higher temperature.

The influence of calcination holding time on iron removal was performed in the range of 0.5-2.5 h. The results are shown in Figure 8. The iron removal rate increases rapidly with an extension of holding time. At 0.5 h 68 % of iron removal was observed, while for 4-fold longer time (2.0 h) a 74 % of iron removal was found. Further increase in time has no significant improvement in the iron removal efficiency. Therefore, the holding time of 2.0 h is opted as the best one.
3.6. COMPREHENSIVE CONDITION EXPERIMENT

3N level high purity quartz product was obtained under the optimal parameters, i.e., a calcination temperature of 900 °C, a calcination holding time of 2 h, a oxalic acid concentration of 10 g/L, a hydrochloric acid concentration of 5 %, a extraction temperature of 60 °C, a liquid solid ratio of 5, a ultrasound power of 400 W and a ultrasound treatment time 30 min. SiO₂ content was increased from 99.6828 % to 99.9047 %, Fe₂O₃ content reduced from 0.0857 % to 0.0223 %, and a maximal iron removal rate up to 74 %. The chemical composition of concentrate is shown in Table 2.

3.7. EFFECT OF PURIFICATION PROCESS ON PARTICLE SIZE

Figure 9 shows the sample particle size distribution analysis. The size of the initial quartz sands is between 150 and 350 μm with the average particle size of 238 μm (Fig.9A). Figure 9B shows the sample particle size distribution after conventional acid leaching with the average particle size of 234 μm, which is very similar to the initial sample because only 4 μm decrease. The particle size distribution of the sample after ultrasound-assisted acid leaching is shown in Figure 9C and has an average particle size of 216 μm. A 22 μm decrease in particle size can be observed in comparison to the initial one. This result is consistent with the analysis of section 3.4, because the ultrasound cavitation and the combination of ultrasound and acid leaching promotes the quartz particles become more porous and even in some cases can break down. Figure 9D shows the particle size distribution of sample after calcination pretreatment and ultrasound-assisted acid leaching. The average particle size is 200 μm, which is 38 μm lower than that of the initial one. This result is also in agreement with the results presented in section 3.5 because the volume changes caused by the crystal transformation lead to the particles size reduction by their breaking down.

3.8. EFFECT OF PURIFICATION PROCESS ON MICROSTRUCTURE

Figure 10 depicts SEM micrographs of samples. As it can be seen in Figure 10A, many small particles are adhered to or inlaid with the quartz particle surface and they can be considered as impurities. After the conventional acid leaching, a number of small particles adhered to the quartz particle surface is
Table 2 The chemical composition of concentrate samples (%).

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>99.9047</td>
<td>0.0810</td>
<td>0.0223</td>
<td>0.0106</td>
<td>0.0194</td>
<td>0.0189</td>
<td>0.0213</td>
</tr>
</tbody>
</table>

**Fig. 9** Particle size distribution of (A) Original samples, (B) Leached solid samples, (C) Ultrasound-assisted leached solid samples and (D) Calcination pretreatment + ultrasound-assisted leached solid samples (Calcination conditions - temperature: 900 °C, holding time: 2 h. Acid leaching conditions - OA concentration: 10 g/L, HCl concentration: 5 %, temperature: 60 °C, L/S: 5, stirring speed: 500 rpm. Ultrasound conditions - power: 400 W, time: 30 min).

lower. This may indicate that these impurities were partially dissolved in acid solution (Figure 10B). Figure 10C shows the ultrasound-assisted acid leaching sample in which almost all small particles disappeared. This is because a strong wave of ultrasound force can peel off impurities adhered on the quartz particle to the acid solution, which promoted further reactions. It can be observed that ultrasound treatment is more effective to remove iron impurities from the surface of quartz than conventional leaching. The maximum iron removal rate is 64 %, which means that the remaining iron impurities are difficult to be removed from the quartz sand lattice. The morphology of the quartz particle surface in Figure 10D (calcination pretreatment + ultrasound-assisted acid leaching testing sample) is similar to that in Figure 10C, but the iron removal rate increased to 74 %. This is due to rapid changes in temperature (calcination and water quenching treatment), which promoted the quartz particles disruption, so the internal impurities are exposed and reacted with the acid solution. Hence iron removal rate was improved.

3.9. **EFFECT OF PURIFICATION PROCESS ON GAS-LIQUID INCLUSIONS**

Figure 11 demonstrates polarized light microscope images of analyzed samples. The gas-liquid inclusions inside quartz particle are smaller and mostly of micron-level (Fig. 11A). The conventional acid leaching can only remove impurities from the surface of particle, hence it is ineffective in the
Fig. 10 SEM images of (A) Original samples, (B) Leached solid samples, (C) Ultrasound-assisted leached solid samples and (D) Calcination pretreatment + ultrasound-assisted leached solid samples (conditions of samples are same as those described in Figure 9).

removal of the gas-liquid inclusions as still some obvious inclusions can be seen in Figure 11B. It is apparent that the volume of the gas-liquid inclusions in the quartz particle after ultrasound-assisted acid leaching get smaller (Fig. 11C) and the ultrasound plays the bursting effect on the particles leading to the large volume of the gas-liquid inclusions to break. Relatively small gas-liquid inclusions can be still observed in Figure 11C. This indicates that ultrasound crushing of quartz particles is limited and failed to make smaller gas-liquid inclusions rupture. Figure 11D shows the polarized micrograph of the sample after calcination pretreatment + ultrasound-assisted acid leaching. It can be clearly seen that the volume of the gas-liquid inclusions is the smallest in this case. During the process of large volume of gas-liquid inclusions burst into small inclusions and consequently the iron impurities released from the inclusions can be dissolved in acid solution, so iron impurities can be further removed.

4. CONCLUSION

A harmless purification method of industrially quartz has been proposed. This method, calcination pretreatment combined with ultrasound-assisted by a mixture of oxalic acid and diluted hydrochloric acid leaching, was proven to be an effective way for iron removal from quartz. Under the optimal technological parameters, i.e., a calcination temperature of 900 °C, a calcination holding time of 2 h, a oxalic acid concentration of 10 g/L, a hydrochloric acid concentration of 5 %, a extraction temperature of 60 °C, a liquid solid ratio of 5, a ultrasound power of 400 W and a ultrasound treatment time 30 min, SiO₂ content of concentrate increased from 99.6828 % to 99.9047 %, and Fe₂O₃ content reduced from 0.0857 % to 0.0223 %, which achieved 3N level high purity quartz. The novel method is more effective than other conventional processes and undesired second pollutions are avoided thus the proposed method is much more environment-friendly than currently known.

REFERENCES


Fig. 11  Polarized light microscope images of (A) Original samples, (B) Leached solid samples, (C) Ultrasound-assisted leached solid samples and (D) Calcination pretreatment + ultrasound-assisted leached solid samples (conditions of samples are same as those described in Fig. 9).


