Physico-Chemical Study of Silica Rocks from the East Coast Malaysia Region for Crystal Glass Application

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Abstract: The main objective of the current work is to recover SiO2 various acid concentrations, scrubbing time, and attrition impeller speed for crystal glass application. Silica rocks were treated using a physico-chemical method involving physical separation method using citric and sulphuric acids as the reagents. Low acid concentration range of 1%-2% and variable scrubbing time of 10, 20, and 30 min were investigated. The microstructure, phase, and particle size of the silica rocks were determined after scrubbing process. Citric acid was found effective in improving the purity of SiO2 to 99.8% at 0.75% concentration, via a 20 min scrubbing process operated at 1,250 rpm (rotations per minute). The phase structure and morphology of the recovered SiO2 were confirmed as trigonal crystal structure with small and irregular shape. To date, studies on the processing of silica rock using organic acid are yet very limited.

Key words: Silica rocks, acid concentration, citric acid, attrition scrubber.

1. Introduction

The silica rock of study originates from a quartz ridge covering an area of 5 km² located in the southern part of Lojing, which is about 4 km southwest to the town of Gua Musang. The quartz ridge or dyke is believed to be a late phase magma residue that penetrated the weak zone of the boundary between the Gua Musang Formation and the Silur-Devon metamorphic rock in the Late Triassic period [1, 2].

The average content of SiO2 is 98.1% with minor presence of Fe2O3, Al2O3, and TiO2, at average contents of 0.1%, 0.4% and 0.01% respectively. An estimated silica rock reserve of 6.67 million metric tons has been identified in the area. Silica utilization is very important in various applications such as ceramic products, electronic components, and additives in concretes. However, the major application of silica is dominated by the glass industry. A previous research reported the successful improvements of the clarity and properties of crystal glass using local sand with 99.5% silica content and less than 0.1% iron content from Gong Belibis Setiu, another potential silica sand from Bintulu was found suitable for tableware application based on its contents of 99.7% silica and 0.01% iron [3, 4].

According to the Malaysia Standard, MS 701:1981 specification, commercial sand for crystal glass making should meet the grade B specifications in which the purity of the silica sand is not less than 99.5% with only small amounts of iron oxide (0.015%), alumina (0.05%), chromium oxide (2 ppm), and titanium oxide (0.05%) being present [5].

To enhance the purity of silica, several approaches were suggested in the literatures, including attrition scrubbing process, wet high intensity magnetic separation (WHMIS), and biological treatment [6, 7]. Among all the methods available, attrition scrubbing is deemed the simplest and the most economical process. In this paper, study on the attrition scrubbing process using organic acid as the reagent is presented concerning the awareness towards health and environment.

The advantages of organic acid are: it is very selective, its acid plants require low capital cost, it poses less environmental hazards, and it is a
biodegradable acid. Organic acids such as citric, acetic, and oxalic acids are the new attractive and alternative eco-friendly reagents used for metals removal technology owing to their excellent biodegradability. Organic acid could dissolve metals by supplying both protons (i.e. acidolysis) and metal-complexing anions (i.e. complexolysis) into the metal ion environment [8].

2. Methodology

2.1 Field Investigation

Fig. 1 shows the location of the silica rock distribution in Gua Musang. The estimated area of surface potential of silica rock is about 34.69 acres. Outcrop mapping and rock block mapping were carried out via transverse methods using compasses, measuring tapes, GPS devices, and topographic maps into a 1:50,000 scale base map. A total of 18 rock samples were collected from each potential area and transported to laboratory.

The sampling was done using a hammer, jack hammer, and pionjar drill tool to obtain fresh and suitable rock samples. GPS devices were used to determine the location and the height of the area where the volume of silica rock can be roughly estimated. The total volume of silica rock within the area was 2.52 million cubic m$^3$. Considering the density of a silica rock to be 2.65 g/cm$^3$, the total measured reserve of silica rock in that area was approximately 6.67 million tonne.

Minus 600 µm fraction of the silica rock samples was collected by sieving process. A complete chemical analysis was carried out on the original sample using Shimadzu XRF-1700 instrument. Phase analysis was conducted on the raw and post treatment samples via X-ray diffraction (XRD) using D8 Advance instrument, Bruker. Field Emission Scanning Electron Microscopy (FESEM) was also employed for morphological and mineral phase identification. In total 70% of solid scrubbed particles was used in this analysis. Minor elements Fe$_2$O$_3$ quantifications were made on silica sample by using a Perkin Elmer Lambda 25 ultraviolet-visible (UV-VIS).

Physico-chemical study was carried out using attrition scrubbing process. Optimization of the attrition process was made by investigating the effects of acid concentration, type of acid, attrition scrubbing time, and attrition impeller speed.

3. Results & Discussion

The result of chemical analysis on the raw silica rock is as illustrated in Table 1. The raw sample composed of 98.75% SiO$_2$, 0.410% Fe$_2$O$_3$, 0.175% TiO$_2$, and 0.492% of other compositions. A high grade silica must contain 99% SiO$_2$ or above and is free of inclusions, coating, and stains of any heavy mineral [9].

Acid concentration was varied at four concentration levels of 0.25%, 0.75%, 1.5%, and 2%. The recovery percentage of silica increased by a maximum of 1.12% with C$_6$H$_8$O$_7$ addition at 0.75% concentration as displayed in Fig. 2. This is attributed to the increasing concentration of complexing ions such as citrate or oxalate which increases the soluble fraction. However, a decrease in the purity of SiO$_2$ was observed with further increase of C$_6$H$_8$O$_7$ concentration than the optimum which can be explained by the diffusion rate factor.

This phenomenon may be due to the collapse of the SiO$_2$ structure at concentrations beyond the optimum [10]. The diffusion rate of SiO$_2$ ions from solid into the solution increases as the concentration and diffusion rate of hydronium ions rise; until a maximum recovery was reached at 0.75% C$_6$H$_8$O$_7$. It can be observed that higher acid concentrations did not improve the silica rock composition.

In this study, sulphuric acid solution was also used as a reagent in the attrition scrubbing process. At the similar concentration of 0.75%, 99.77% of SiO$_2$ recovery was achieved which is significantly lower compared to 99.87% recovery by C$_6$H$_8$O$_7$. A higher concentration of sulphuric acid is needed to achieve higher SiO$_2$ recovery.
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Fig. 1  Location map of the Gua Musang District, Kelantan.

Table 1  Chemical compositions of the raw and treated silica rocks.

| Compound | Raw material composition (%) | Composition after C\textsubscript{6}H\textsubscript{8}O\textsubscript{7} treatment (%) |
|----------|-----------------------------|---------------------------------|
| SiO\textsubscript{2}     | 98.75                       | 99.87                           |
| Fe\textsubscript{2}O\textsubscript{3} | 0.410                       | 0.114                           |
| Al\textsubscript{2}O\textsubscript{3} | 0.175                       | -                               |
| TiO\textsubscript{2}     | 0.067                       | -                               |
| Others          | 0.492                       | 0.026                           |
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Fig. 2 Effect of acid concentration on the silica yield (%).

However, the effectiveness difference between both C₆H₈O₇ and sulphuric acid reagents is only around 0.1%, thus signifying the later as acceptable and effective. In addition, the fact that C₆H₈O₇ is an organic acid could attribute to the slight difference in recovery efficiency.

3.1 Scrubbing Time

The silica yield improved to an optimum of 99.87% using an attrition scrubber operated at 1,250 rpm for 20 min (Fig. 3). The SiO₂ content was decreased by 1.5% with further increase in attrition time beyond optimum where no remarkable improvement in silica content was noticed. The silica rocks achieved Fe₂O₃ concentration (< 0.015 rpm) when scrubbing time increased to optimum scrubbing time. Meanwhile, minor oxides such as Al₂O₃ and TiO₂ were completely removed from the silica rock and the other value is 0.026% (Table 1).

3.2 Attrition Impeller Speed

An improvement in SiO₂ yield by 0.24% was observed with increasing attrition impeller speed from 1,000 rpm to 1,250 rpm (Fig. 4). Higher impeller speed increases the rate and intensity of collisions between SiO₂ and the remaining materials, thus improving the removal of contaminants [11]. However, no further improvement in SiO₂ yield was found when the attrition speed was increased to beyond the optimum (1,250 rpm). This is due to the insufficient difference in relative velocity between particles, which reduces the rate and intensity of collisions. Therefore, the optimum condition of attrition impeller speed was 1,250 rpm with 99.80% of SiO₂ yield achieved.

Fig. 5 displays the XRD diffractograms of the raw and C₆H₈O₇ treated silica rocks. Sharp and high intensity quartz (SiO₂) peaks were observed in both patterns at the positions of 20.860° and 26.640°. The crystalline quartz present has a d-spacing value of P3221 and a crystal structure of trigonal with hexagonal axis (JCDS 00-046-1045).

At 20 of 20.860° and 26.640°, the peak intensities of quartz for the raw silica rock were of 3,526.90 and
Fig. 3  Effect of attrition time on the SiO$_2$ recovery (%).

Fig. 4  Attrition impeller speed (rpm) on the silica yield (%).
28,052.7 counts respectively. However, after the \( \text{C}_6\text{H}_8\text{O}_7 \) treatment, the peak intensities increased to 8,265.90 and 65,675.4 counts respectively at the same 20 positions. Removal of the impurities increased the crystallinity peaks.

This indicates that the purity of silica (\( \text{SiO}_2 \)) in the samples increased after the scrubbing process. As illustrated in Fig. 6, \( \alpha \)-quartz crystal system was observed in the silica rocks with lower atomic spacing than that of the generic quartz crystal structure.

It is evident from the FESEM micrographs in Fig. 7 that the sieved raw silica rock consists of rather spherical particles with a size range of 185.1 \( \mu \text{m} \) to 678.7 \( \mu \text{m} \). While for the silica after treatment, smaller
Fig. 7  FESEM images of (a) silica rock and (b) silica after scrubbing process.

Fig. 8  EDX diffractograms of (a) silica rock and (b) silica after treatment.

Table 2  Composition of raw silica rock from EDX analysis.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| O K     | 53.83      | 67.18      |
| Si K    | 46.17      | 32.82      |
| Cr L    | 0.00       | 0.00       |
| Fe L    | 0.00       | 0.00       |

and irregular crushed particles of silica were noted with a median size of 493.6 µm. The formation of fine irregular shaped particles in the silica after scrubbing with C₆H₈O₇ acid is possibly due to the physico-chemical effect and the decomposition of SiO₂ into finer particles.

Fig. 8 shows the result of EDX analysis of raw silica rock which revealed high weight percentages of silicon and oxygen in the sample, of 46.17 wt.% and 53.83 wt.% respectively. Other than silica, minor amounts of chromium oxide and iron oxide components were detected in the raw silica rock from the EDX analysis (Table 2).

4. Conclusion

The purity of SiO₂ has been successfully increased to 99.76% via a scrubbing process using 0.75% C₆H₈O₇ acid concentration, 20 min of scrubbing time, and 1,250 rpm of attrition scrubbing speed. High intensity peaks of crystalline α-quartz SiO₂ structure were observed from XRD analysis on the silica samples after treatment at 2 theta values of 20.860°
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and 26.640°. FESEM analysis revealed SiO₂ of a significantly smaller and irregular shape formed after the physico-chemical treatment.

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