Properties and behavior of silica rock from east coast Malaysia region in crystal glass application

Syarifah Aminah Ismail[*], Mohd Idham Mustaffar

Mineral Research Centre, Mineral and Geoscience Department Malaysia, Jalan Sultan Azlan Shah, 31400 Ipoh, Perak, Malaysia
*Corresponding author: syarifahaminah@jmg.gov.my, idham@jmg.gov.my

Abstract

Crystal glass is defined as colorless and translucent glass, which is generally applied as tableware utensils and art products, in compliance with the ASTM C162-56 standard method. Traditionally, crystal glass was manufactured using silica sand with SiO_2 purity of not less than 99.5 %. In this research, local silica rock acquired from the east coast of Malaysia region was utilized in the production of crystal glass. Previous studies revealed that raw silica rocks possess a good quality, but still inadequate to comply with the minimum requirements for crystal glass making. The purpose of this study was to improve the quality of silica rock via a physico-chemical method that comprised simultaneous attrition scrubbing and acid treatment. In this method, variable citric acid concentrations of less than 1 %, and constant scrubbing time and speed of agitation of 20 minutes and 1250 rpm, respectively were implemented. Markedly, citric acid was found effective in improving the purity of SiO_2, where 99.8 % purity was successfully achieved at 0.75 % acid concentration. XRD analysis revealed trigonal crystals system of SiO_2 in the silica rock samples. By implementing the novel crystal glass formulation, crystal glass with density of ≥ 2.40 g/cm^3, Vickers hardness of 550 ± 20 kg.f/cm^2, and refractive index of ≥ 1.5 was successfully produced, which complied with the standard requirements of BS 3828:1973.

1. Introduction

Glass is an important material owing to its attractive appearance and versatile usage. The main composition of glass includes sand, lime (alkaline earth oxide), sodium or potassium oxide (alkali oxide) and other elements, where each component has its own contribution to the overall properties of the glass. Particularly, potassium contributes to enhance the light refraction and transparency of glass, making it more appealing. In addition, zinc is commonly added into the composition for chemical durability and safety in the glass products. In general, glass is categorized into four distinct groups, namely borosilicate, glass, crystal glass, and lead crystal. Composition in crystal glass, which contains 10 % of metal oxides, is highly priced due to the quality of its raw material. Small impurities such as iron could affect the crystal glass color, hence high purity sand (silica oxide) is commonly used to over-come this drawback. The crystal glass from local silica sand has been reported with hardness values between 517 kg./cm^2 to 520 kg./cm^2 (Mohamad Haniza Mahmud and Abdul Hadi Abdul Rahman, 2016), which are still acceptable but it requires improvement for crystal glass quality. In enhancing the properties of silica, several methods were suggested in the literature, including the use of ultrasound for surface cleaning of silica (Farmer and Jameson, 2000), acid leaching (Khalifa and Ezzaouia, 2019), and reverse flotation technique (Yuan and Chen, 2018).

In this current research, crystal glass from local silica rock which is from argillaceous rock, volcanic and limestone formation was prepared via a physico-chemical method using low concentrations of organic acid (less than 1%). Attrition scrubbing was conducted with citric acid as the chelating agent, which has the capability to recover silica content and remove

impurities such as iron. Moreover, in comparison to other conventional acids, e.g. sulfuric acid, hydrochloric acid, or nitric acid, the cost of citric acid is much lower (Bouabdallah and Chaib, 2015). Citric acid is a natural acid with low molecular weight. It is considered as a non-persistent biodegradable product (Romkens and Draaisma, 2002) with a half-life in soil suspension of close to 8 days (Brynhildsen and Rosswall, 1997). These characteristics make citric acid as potentially the sole medium for the effective recovery of silica oxide even at a concentration as low as 0.05 mol/L, with no risk for pollution or post-treatment requirement (Larba and Tifouti, 2013).

However, to the best of the authors' knowledge, no studies are available concerning the use of silica rock for crystal glass fabrication. In view of that, this present work reveal the implementation of a new source of silica rock from the east coast Malaysia region for crystal glass manufacturing, by considering its lower density, refractive index, and Vickers hardness than those of silica sand.

2. Methodology

2.1 Field investigation and sample collection

Fig. 1 shows the maps of silica rock deposit for this study located in Lojing, Gua Musang, Kelantan. The potential silica rock deposit an area of about 34.69 acres. Outcrop mapping and rock blocking were carried out using transverse methods with the aid of compasses, measuring tapes, GPS devices, and topographic maps (1:50,000 scale to base map). Based on visual observation, the silica rock samples were characterized with light greyish color and rough surface, as illustrated in **Fig. 2**. Different quartz colorations were observed due to various contents of SiO_2 and impurities. Gua Musang formation comprises of argillaceous rock, volcanic and limestone. The quartz ridge or dyke is believed to be a late phase magma residue that intruded into metasedimentary rocks and shifted by fault zone at the boundary between the Gua Musang Formation and the Silurian-Devonian metamorphic rock in the Late Triassic period (Ngah, 1986 and Foo, 1973).

2.2 Experimental work

In this study, 30 kg of silica rock samples was collected from Lojing in Gua Musang, Kelantan. The samples were analyzed using X-ray fluorescence (XRF) in order to identify the elemental composition prior to attrition scrubbing treatment. From the analysis, the samples showed the presence of SiO_2, Fe_2O_3, Cr_2O_3, and Al_2O_3 (Table 2). The process of attrition scrubbing is commonly employed for ion reduction instead of SiO_2 content enhancement. However, this process is important since the presence of Fe_2O_3 and other impurities could influence the quality of crystal glass. (Nishkov and Grigorova, 2011).Therefore, an optimization of the final product of crystal glass after attrition scrubbing process was carried out in this study.

The silica rock samples were sieved in order to obtain a fraction of particle size that is less than 600 µm. The samples were subsequently subjected to attrition scrubbing operation using a laboratory "Denver flotation cell" with a Perspex container, as shown in **Fig. 3**.

Optimization of the scrubbing process was performed by studying the effect of varying acid concentrations. The scrubbed silica rocks were deslimed and thoroughly washed using water prior to mixing for palletizing processes. In this study, the crystal glass formulation employed is shown in Table 1.

Table 1: Crystal glass formulation

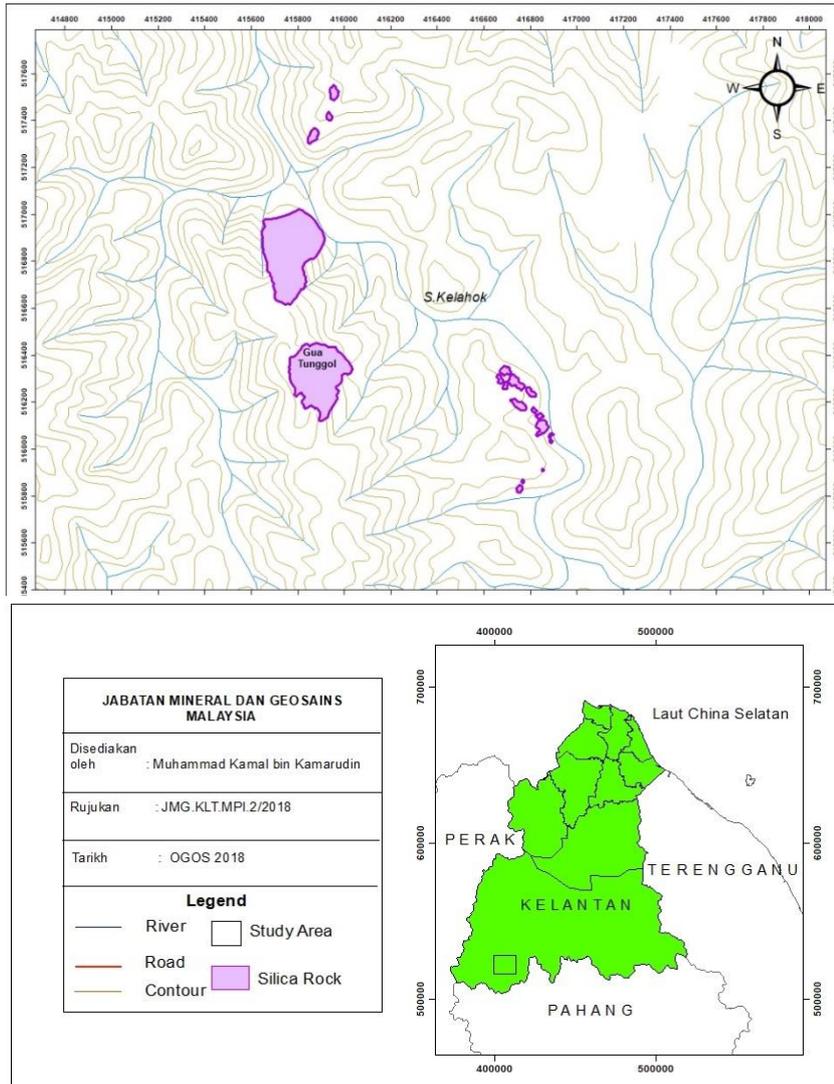| Component	Percentage
SiO_2	60-65
Na_2O	11-4
K_2O	6-8
BaO	6-8
Ba_2O_3	1-4
CaO	7-10
Sb_2O_3	1-3
Al_2O_3	1-3
Na_2SiO_3	2-5

Fig. 1: Maps of silica rock deposit intruded into Gua Musang Formation in Lojing, Kelantan

Fig. 2: Coarse-grained light grey silica rock

Fig. 3: Assembled impeller system

A complete chemical analysis was carried out on the raw silica rock samples using X-ray fluorescence (XRF), Shimadzu XRF-1700 instrument. Meanwhile, phase analysis was conducted on the raw and post-treatment samples via X-ray diffraction (XRD) using D8 Advance instrument, Bruker.

3.1 Phase identification

Fig. 4 illustrated XRD pattern of the raw silica rock. The characteristic peak of α-quartz (JCDS 00-046-1045) appeared as the major constituent, confirming its abundant content in crystallized silica rocks within the east coast Malaysia region. The intense peaks at 2θ = 20.860° and 26.640° indicated the presence of crystalline silica in the sample. Furthermore, the raw silica rock, which was free from any treatment, was characterized with trigonal silica phase.

3.2 Chemical composition

Major elemental quantification was made on 18 samples of silica rock through XRF analysis. The chemical composition of the silica rock (Table 2) revealed high and consis--tent percentages of SiO_2 with an average of over 98.12 wt. %, indicating the quartz-rich nature of the samples. The silica rock was characterized with low percentages of alumina (Al_2O_3) and manganese oxide (MnO) of <0.41 wt.% and <0.01%, respectively. These properties were indicative of the extra-siliceous content within the silica rock (Tsai, 2004). Minor oxides of Fe_2O_3, Na_2O, K_2O, and TiO_2 also presented at low percentages which was not exceeding 0.6 wt. %. For this chemical analysis, the average loss on ignition (LOI) value was 0.30%.

3.3 Attrition scrubbing of the silica rock sample

3.3.1 Effect of acid concentration

Table 3 illustrated the chemical analysis of the raw silica rock. The raw sample composed of 98.75% SiO_2, 0.410% Fe_2O_3, 0.175% TiO_2, and 0.492% of other compounds. As commonly reported, a high-grade silica must contain 99% or above SiO_2 and is free of inclusions, coating, and stains of any heavy mineral (Andrews, 1984).
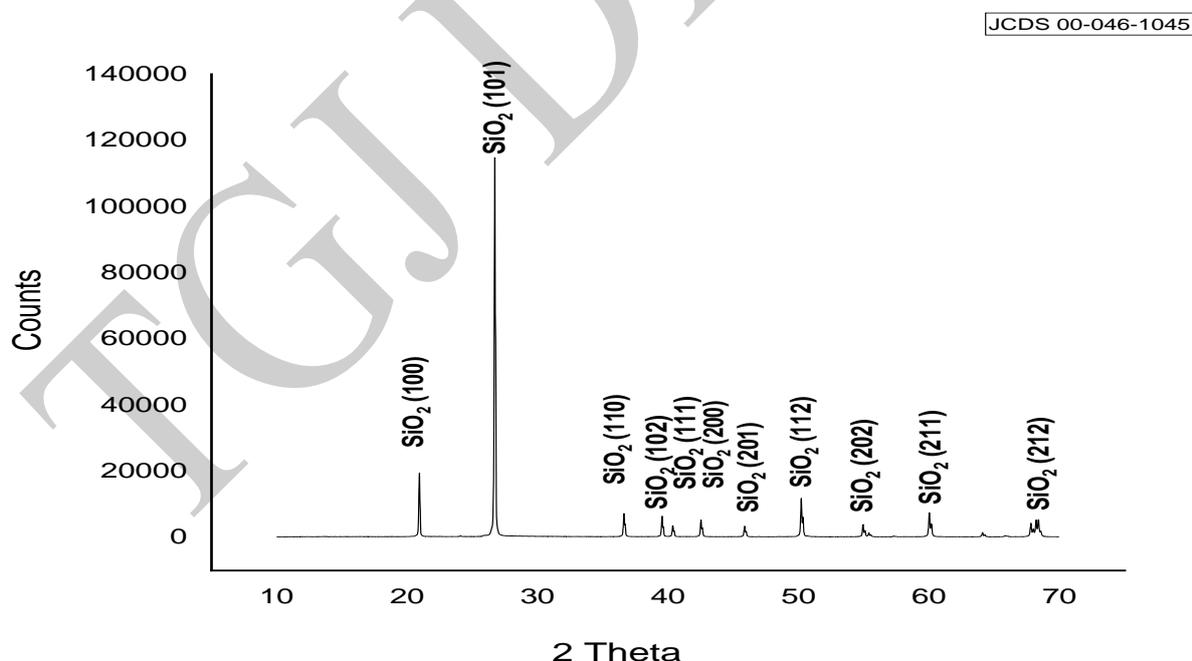

Fig. 4: XRD pattern of the raw silica rock sample

Table 2: Chemical composition of the raw silica rock sample

Sample No.	Chemical Composition										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	MgO	CaO	MnO	P_2O_5	LOI
1	98.00	0.57	0.09	<0.01	0.12	<0.01	0.05	<0.01	<0.01	0.01	0.31
2	98.00	0.60	0.06	<0.01	0.13	<0.01	0.05	0.01	<0.01	0.02	0.29
3	98.20	0.55	0.07	<0.01	0.09	<0.01	0.04	<0.01	<0.01	0.01	0.22
4	96.90	1.07	0.22	<0.01	0.27	0.01	0.08	<0.01	<0.01	0.02	0.40
5	96.90	1.01	0.06	0.01	0.27	0.02	0.08	<0.01	<0.01	0.01	0.39
6	98.10	0.60	0.22	<0.01	0.10	0.01	0.06	<0.01	<0.01	0.01	0.28
7	98.90	0.24	0.04	0.02	<0.01	0.01	0.03	<0.01	<0.01	0.02	0.35
8	99.00	0.23	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.08
9	99.00	0.24	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.22
10	98.70	0.27	0.04	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.14
11	99.10	0.22	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.11
12	98.70	0.35	0.07	<0.01	0.02	0.01	0.03	<0.01	<0.01	0.01	0.20
13	98.90	0.26	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.19
14	99.00	0.25	0.02	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.02	0.33
15	98.60	0.39	0.14	<0.01	0.05	<0.01	0.05	0.01	<0.01	0.01	0.28
16	96.20	0.27	0.29	0.08	0.01	0.01	0.32	0.16	<0.01	0.02	0.75
17	96.90	0.17	0.30	0.02	0.02	0.05	0.08	0.03	<0.01	0.01	0.33
18	97.00	0.04	0.14	0.05	<0.01	0.03	0.25	0.02	0.01	0.01	0.47
Avg.	98.12	0.41	0.10	0.04	0.11	0.02	0.07	0.05	0.01	0.02	0.30

Table 3: Chemical compositions of the raw and treated silica rocks

Compound	Raw (%)	$C_6H_8O_7$ treated (%)
SiO_2	98.75	99.87
Fe_2O_3	0.410	0.114
Al_2O_3	0.175	-
TiO_2	0.067	-
Others	0.492	0.026

In this research work, acid concentration was varied at five concentration levels i.e. 0.25%, 0.5%, 0.75%, 1.0 %, and 1.5%. The maximum recovery of silica was achieved at 99.87 % with 0.75% $C_6H_8O_7$ addition, as displayed in **Fig. 5**. This condition was attributed to the increasing concentration of complex ions such as citrate or oxalate, which increased the soluble fraction. However, a decrease in the purity of SiO_2 was observed with a further increase in $C_6H_8O_7$ concentration than the optimum, which can be explained by the diffusion rate factor.

This scenario was due to the collapse of the SiO_2 structure at concentrations beyond the optimum (Al-Zahrani, 2009). The diffusion rate of SiO2 ions from solid into the solution increased as the concentration and diffusion rate of hydronium ions increased, until a maximum recovery was reached at 0.75 % $C_6H_8O_7$. Recovery of SiO_2 purity decreased from 99.87% to 98.73% when reached at 1% $C_6H_8O_7$. It can be observed that a further increment of the acid concentration did not improve the purity of the silica (Shin and Lee, 2014).
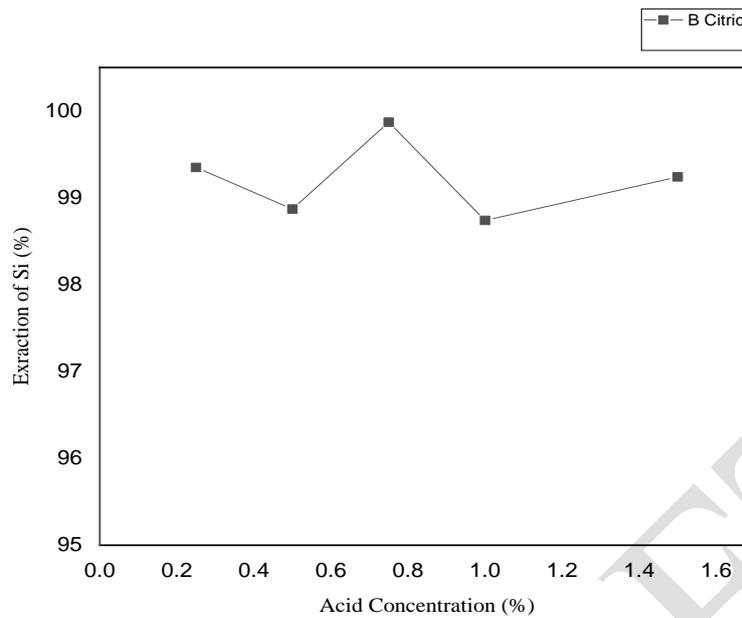
Fig. 5: Effect of acid concentration on silica recovery

3.4 Crystal glass properties

3.4.1 Refractive index

Five samples, namely Sample A, Sample B, Sample C, Sample D, and Sample E represent the silica rock samples treated using various acid concentrations of 0.25%, 0.5%, 0.75%, 1.0 %, and 1.5%, respectively. The refractive indices of all samples, as well as the raw silica rock, were as indicated in Table 4. The difference in the values of refractive index amongst particular crystal glass was influenced by the purity of SiO_2 composition and the content of metallic oxides. In general, the refractive index of the crystal glass from the silica rock was higher than ≥ 1.50, thus fulfilling the specification for crystal glass application in accordance to the BS 3828:1973.

Table 4: Refractive index, density, and Vickers hardness of different crystal glass types

Acid concentration (%)	Refractive Index	Density (g/cm^3)	Vickers hardness kg.f/cm^2
Raw sample	1.5280	2.5949	486.0300
Sample A	1.5274	2.6273	437.2000
Sample B	1.5258	2.6298	414.2200
Sample C	1.5261	2.6326	466.7000
Sample D	1.5273	2.6180	483.9000
Sample E	1.5240	2.6130	476.2700

3.4.2   Density

As specified in the BS 3828:1973, there are four (4) accepted values of density of crystal glass, which are based on the percentage of metallic oxides. A full lead crystal (30% lead oxide content) should have a density of greater than or equal to 3.00 g/cm3, while an acceptable crystal glass with the lowest content of lead oxide (less than or equal to 10%) is classified with a minimum density value of 2.40 g/cm3. The results of the density tests were summarized in Table 4, where all the density values were in the range of full lead crystal and crystal glass with at least 10% of BaO, PbO, and K_2O contents, either individually or grouped. In other words, the crystal glass produced from scrubbed silica rock demonstrated a comparable crystal glass specification by BS 3828:1973. However, the difference in the density value was due to several factors including the structure, bonding, and chemical composition of the glass material itself (Schubert, 1997). Furthermore, the density properties of the crystal glass were also influenced by the cooling process. Rapidly cooled samples exhibited slightly lower density values as compared to the slowly cooled samples, as a result of less melting time needed to densify its structure upon freezing.

3.4.3   Vickers hardness

Table 4 presented the Vickers hardness of Sample A, Sample B, Sample C, sample D, and Sample E. From the results, it can be concluded that the hardness of the crystal glass produced from east coast Malaysian silica rock is lower within the range of 414.22 kg.f/cm2 to 486.03 kg.f/cm2 than the required hardness by the BS 3828:1973 of 550 ± 20 kg.f/cm2. It was concluded that the crystal glass produced from silica rock was comparatively softer than that fabricated from traditional silica sand (Mohamad Haniza Mahmud and Abdul Hadi Abdul Rahman, 2016). Moreover, the surface hardness of the glass could generally affect the cutting and engravement process.

4.   Conclusion

The properties and behavior of the silica rock acquired from the east coast of Malaysia region were investigated in the application of crystal glass. The maximum SiO_2 content of 99.76% of the silica rock samples was achieved from a purification process using 0.75% $C_6H_8O_7$ acid concentration with 20 minutes of scrubbing time, and attrition scrubbing agitation of 1250 rpm. The silica rock meet the grade B specification in which the purity is more than 99.5% with small amount of impurities such as iron oxide (0.015%), alumina (0.05%), chromium (2ppm) and titanium oxide (0.05%). Intense peaks of crystalline structured corresponding to α-quartz were observed from the XRD analysis on the treated silica rock at 2θ of 20.860º and 26.640º accordingly. The studied silica rock was found suitable for crystal glass application, at the provided density ($\geq$ 2.40 g/cm3), Vickers hardness (550 ± 20 kg.f/cm2) and refractive index ($\geq$ 1.5) and were in compliance with the standard requirements of BS 3828:1973.

References

Al-Zahrani, A. A. (2009). Extraction of alumina from local clays by hydrochloric acid process. *Engineering Sciences*, *20*(2).

Andrews, W. H. (1984). Uses and Specifications of Silica sand. *Res. Counc. Alberta, Bull.; (Canada)*, *71–4*, 49–66.

Bouabdallah, S., Bounouala, M., Idres, A., & Chaib, A. (2015). Iron removal process for high-purity silica production by leaching and magnetic separation

technique. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, *5*, 47–52.

Brynhildsen, L., & Rosswall, T. (1997). Effects of metals on the microbial mineralization of organic acids. *Water, Air, and Soil Pollution*, *94*(1), 45–57. https://doi.org/10.1007/BF02407092

Farmer, A. D., Collings, A. F., & Jameson, G. J. (2000). The application of power ultrasound to the surface cleaning of silica and heavy mineral sands. *Ultrasonics Sonochemistry*, *7*(4), 243–247. https://doi.org/10.1016/S1350-4177(00)00057-2

Foo, K. Y. (1973). *Summary of The Geology and Mineral Resources the State of Kelantan*.

Khalifa, M., Ouertani, R., Hajji, M., & Ezzaouia, H. (2019). Innovative technology for the production of high-purity sand silica by thermal treatment and acid leaching process. *Hydrometallurgy*, *185*, 204–209.

Larba, R., Boukerche, I., Alane, N., Habbache, N., Djerad, S., & Tifouti, L. (2013). Citric acid as an alternative lixiviant for zinc oxide dissolution. *Hydrometallurgy*, *134–135*, 117–123. https://doi.org/10.1016/j.hydromet.2013.02.002

Mohamad Haniza Mahmud, Mohd Idham Mustaffar, & Abdul Hadi Abdul Rahman. (2016). Development of Lead Free Crystal Glass Using Silica Sand from Gong Belibis Setiu, Terengganu. *Journal of Geological Resource and Engineering*, *4*(3), 137–141. https://doi.org/10.17265/2328-2193/2016.03.004

Ngah, D. S. (1986). *Potential Mineral Resources in Kelantan*.

Nishkov, I., Valchev, A., Marinov, M., Grigorova, I., & Nishkov, I. (2011). *Low Iron Silica Sand for Glassmaking*. *III* (January 2011), 755–760. https://www.researchgate.net/publication/306056275

Römkens, P., Bouwman, L., Japenga, J., & Draaisma, C. (2002). Potentials and drawbacks of chelate-enhanced phytoremediation of soils. *Environmental Pollution (Barking, Essex : 1987)*, *116*(1), 109–121. https://doi.org/10.1016/s0269-7491(01)00150-6

Schubert, U. (1997). Book Review: Introduction to glass science and technology. By J. E. Shelby. *Angewandte Chemie International Edition in English*, *36*(20), 2248–2249. https://doi.org/10.1002/anie.199722481

Shin, D., Jeong, J., Kim, B., Ilyas, S., & Lee, J. (2014). Lead trace removal from waste electronic scraps by organic acids. *Materials Transactions*, *55*(3), 586–590.

Tsai, M. S. (2004). The study of formation colloidal silica via sodium silicate. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, *106*(1), 52–55. https://doi.org/10.1016/j.mseb.2003.08.052

Yuan, Y., Zhang, L., Guan, J., Zhang, C., Wu, J., & Chen, Z. (2018). Contribution on fluid inclusion abundance to activation of quartz flotation. *Physicochemical Problems of Mineral Processing*, *54*.