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Decomposition of spodumene mineral in granitic rocks from South Kalimantan - Indonesia by potassium sulphate

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Abstract. The decomposition behaviour of spodumene mineral in granitic rock from Kalimantan Indonesia by using potassium sulphate has been studied in this research. The granitic rock from Kalimantan is indicated to contain spodumene mineral. The ssodumene is one of the main minerals which contains lithium. The purpose of this study is to decompose the α -spodumene mineral in the granitic rock of Kalimantan to β -spodumene which is subsequently easier to be dissolved in water. In this study, the decomposition of α -spodumene was performed under variations of roasting temperatures (i.e. 350°C, 450°C, 550°C, 600°C, 700°C, 800°C, 900°C and 1000°C) and roasting times (20 min, 40 min and 60 min). The results of the decomposition products were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). It was identified that the granitic rock from Kalimantan consists of α -spodumene ($\text{LiAlSi}_2\text{O}_6$) with lithium content of 3.09 ppm and the other major minerals are quartz (SiO_2) and albite ($\text{NaAlSi}_3\text{O}_8$). The α -spodumene was completely converted to β -spodumene at 700°C for 60 minutes.

1. Introduction

Indonesia is a country that has been blessed with abundant mineral resources, part of them are igneous rocks such as granitic rock [1]. Granite is a bright colour igneous rock which forms from slow crystallization of magma under the surface of the earth. Granite mainly consists of quartz (SiO_2) and feldspar (KAlSi_3O_8 – $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$) as well as small amount of mica ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), amphiboles ($\text{Ca}_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Al},\text{Si})_8\text{O}_{22}(\text{OH})_2$) and spodumene ($\text{LiAlSi}_2\text{O}_6$). The content of spodumene mineral in granitic rocks leads to the interest of granitic rock utilization since the spodumene contains lithium.

The most important lithium mineral is spodumene, which is generally present together with quartz, feldspar, and mica. Along with brines, spodumene mineral has been considered as one of the major resources used for lithium extraction [2]. In terms of production cost, lithium extraction from brines is still more competitive in comparison to lithium extraction from spodumene, lepidolite and other solid minerals[3]. Various processes for lithium extraction from spodumene ore have been proposed.



Lithium is a light metal that has been utilized in the manufacture of glass, ceramics, and lubricating greases since its discovery in 1817. Lithium currently plays an important role in the high-tech industry and has been used in several fields which includes pharmaceuticals, rechargeable batteries, and electronics. More than 30% of total lithium consumption in 2015 is for batteries and since the year of 2000, lithium consumption increased by around 20% every year. The production of electric vehicle has been drastically increasing in recent years and will continue to grow in the next couple decades; therefore the demands of lithium metals as one of the main components of batteries for electric vehicle will be also increasing [4]. The global production of lithium was estimated to be 35,000 tonnes in 2013 which represents an increase of 6% compared to 2012 [5]. Many studies of lithium extraction have been carried out by several researchers. Barbosa et.al. (2014) have studied the extraction of lithium by means of the chlorination roasting of β -spodumene with temperature range of 1000 to 1100 °C for periods of time of 0 to 180 min [6]. Natasha et.al. (2018) have investigated the decomposition of Schistmica rock from Kebumen, Center Java, Indonesia by using sodium sulfate as decomposition agent [7].

Spodumene occurs naturally in α -phase with a monoclinic structure of the pyroxene type [8]. This structure is resistant to the attack of chemical agents, either gaseous or liquid. Spodumene can be transformed into its β -phase by calcination at 1100 °C [8]. This phase is more reactive and less resistant to ordinary chemical agents [9]. A suitable amount of K_2SO_4 and CaO has been added during the roasting process to avoid the fusion of the roasted product and enhancing the efficiency of lithium extraction [10]. Yan et.al., 2012, have conducted the experimental work by adding appropriate amount of CaO and K_2SO_4 during the roasting process of lepidolite to optimize the extraction of lithium [11].

In this study, the decomposition of α -spodumene in the granitic rock from South Kalimantan was performed under variations of roasting temperatures and roasting duration. Potassium sulfate (K_2SO_4) was used as a decomposition agent. The decomposition of α -spodumene was aimed at transforming alpha (α) phase in the spodumene mineral into beta (β) spodumene phase. The beta-spodumene is expected to be readily soluble in water leaching step which is done after the roasting. During water leaching, lithium is released from spodumene mineral and dissolved in water.

2. Experimental and Method

2.1 Materials and Characterization

The granitic rock sample used in this investigation was obtained from South Kalimantan. Potassium sulfate as decomposition reagent with a specification of pro analysis (P.A) grade was purchased from Merck. The characterization of samples was performed by X-ray fluorescence (XRF), inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray diffraction (XRD). The morphology of raw material and the decomposition products were analysed by Scanning Electron Microscope (SEM).

2.2 Methods

In this study, granitic rock samples from South Kalimantan were crushed with a jaw crusher, milled with a ball mill and sieved to obtain a particle size distribution of -200 mesh. The sample was then analyzed by X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma optical emission spectroscopy (ICP-OES) and scanning electron microscopy (SEM). The decomposition of α -spodumene in the ore sample was carried out by roasting of the mixture of the ore sample and potassium sulfate (K_2SO_4) in the "Carbolite" muffle furnace at various temperatures and roasting times. Prior to the roasting, the ore samples were mixed homogeneously with potassium sulfate with a mass ratio of 1:1. The sample was then analyzed by Simultaneous Thermal Analysis (STA) to determine the temperature range which will be investigated in the decomposition experiments. The STA pattern of the mixture of granitic ore sample and K_2SO_4 is presented in Figure 1. HSC Chemistry software was also used to predict the reaction occurs in the decomposition process, its Gibbs free

energy and equilibrium constant at various temperatures. As can be seen in Figure 1, a mass loss occurs in the mixture of granitic ore and K_2SO_4 as it was heated up to 700°C . Mass removal takes place sharply as the heating was carried out at temperature range of 320°C to 600°C indicated by the appearance of the peak that represent positive enthalpy changes (ΔH). This peak indicates that the reaction between the granitic ore sample and K_2SO_4 is an endothermic reaction. Based on the results of STA analysis and simulation by HSC chemistry software, the authors varied roasting temperatures at 350°C , 450°C , 550°C , 600°C , 700°C , 800°C , 900°C and 1000°C . Meanwhile, the roasting times was varied at 20 min, 40 min and 60 min. The products of decomposition were characterized by XRD, XRF, SEM and Energy Dispersive X-ray Spectroscopy (EDS). The flowsheet of the experimental procedure is summarized in Figure 2.

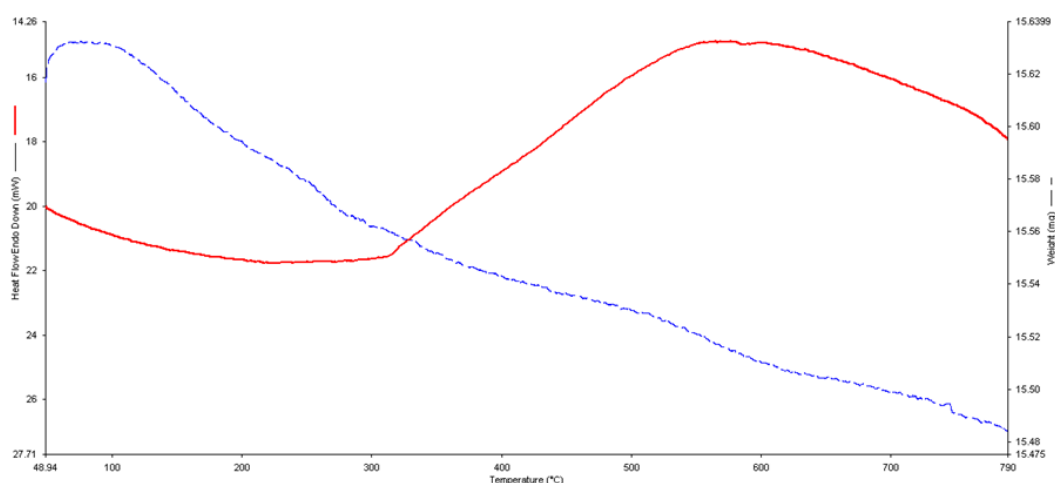


Figure 1. The STA pattern of the mixture of granitic ore sample and K_2SO_4 .

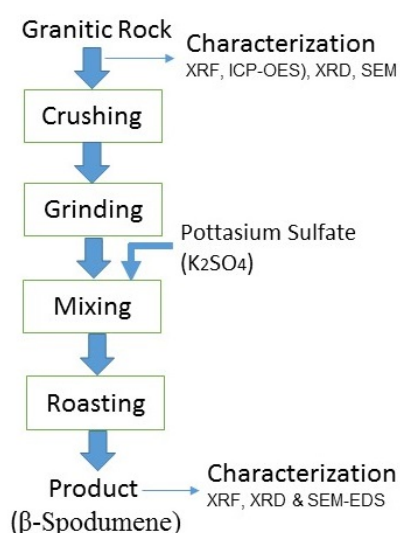


Figure 2. Flowsheet of the decomposition experiment of α -spodumene in granitic ore sample from South Kalimantan.

3. Result and discussion

3.1. Raw Material Characterization

After ore preparation stage, the sample was analyzed by XRF and the analysis result is presented in Table 1. The XRF analysis did not detect the presence of lithium in the granitic ore sample due to its low concentration, therefore, the lithium content was measured by using ICP-OES. The result of ICP-OES analysis showed that the content of lithium in the granitic rock sample from South Kalimantan was 3.09 ppm.

Table 1. The results of elemental analysis of granitic rock sample from South Kalimantan by XRF.

| Element | Mg | Al | Si | P | Cl | K | Ca | Ti | Mn | Fe |
|-------------|------|------|-------|------|------|------|-------|------|------|-------|
| Content (%) | 6.19 | 9.20 | 48.62 | 0.72 | 0.96 | 2.03 | 14.27 | 1.19 | 0.43 | 13.87 |

The result of XRF analysis shows that Si, Ca, Fe, Al, and Mg are the major elements of the granitic rock sample from South Kalimantan. The presence of Si, Al, and Li elements in granitic rock indicates that South Kalimantan's granitic rocks contain lithium mineral as spodumene ($\text{LiAlSi}_2\text{O}_6$) at a fairly small content. Until recently, the data of major source of the lithium-bearing minerals in Indonesia has not yet been clearly reported. In addition to the granitic rock samples from Kalimantan used in this research, the other source of lithium metal in Indonesia is sekismika rock such as that discovered in Kebumen District in Central Java Province [7].

The result of XRD analysis of the ore sample was shown in Figure 3. The XRD pattern shows that the major minerals in granitic rock sample from South Kalimantan are quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$) and α -spodumene ($\text{LiAlSi}_2\text{O}_6$). According to ICSD no. 98-009-0145, quartz can be found at 2θ position of around 23° , 39° , 47° and 55° with a hexagonal crystal system. According to ICSD no. 98-005-2343, albite minerals can be found at 2θ of around 21° , 27° and 28° with anorthic crystal systems. Meanwhile, according to ICSD no. 98-001-0238, spodumene minerals can be found at 2θ of around 14° , 24° , 32° , 36° , 64° and 76° with a monoclinic crystal system. The spodumene-associated peaks appearing at XRD pattern in Figure 3 indicated that lithium mineral was present in the South Kalimantan's granitic rock. This XRD result is in agreement with the result of ICP-OES analysis that measured the content of lithium of 3.09 ppm in the digested ore sample. Results of SEM-EDS analyses of the ore sample are shown in Figure 4 and Table 2.

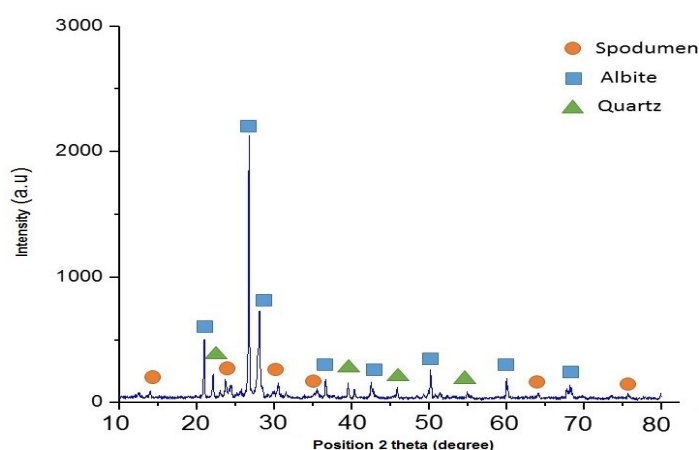


Figure 3. Diffractogram of the granitic ore sample

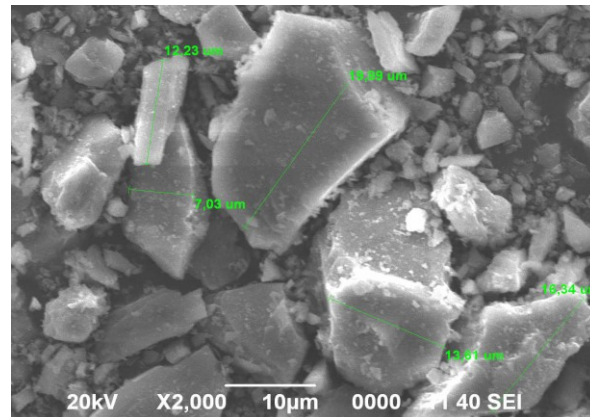


Figure 4. SEM micrograph of the granitic ore sample before roasting.

Table 2. Result of elemental analysis by ZAF Method Standardless Quantitative Analysis of EDS-SEM.

| Element | Mass (%) |
|---------|----------|
| O | 43.54 |
| Mg | 0.46 |
| Al | 1.67 |
| Si | 54.48 |
| Ca | 0.18 |
| Fe | 0.12 |

The SEM micrograph indicates that the morphology of granitic ore has irregular grains with non-uniform grain size. The grain size of the original granitic ore sample is at the range of 7 - 19 μm . The result of EDS-SEM in Table 2 reveals that the major elements within the sample are Si, O and Al. The result of the EDS analysis is in agreement with the result of XRD analysis that detected quartz, albite and spodumene (which contains Si, O and Al elements) as the major minerals in the granitic ore sample from South Kalimantan.

3.2 Effect of roasting temperature

To investigate the effect of roasting temperatures on the decomposition behaviour of the granitic ore sample, the products of decomposition at various temperature with ore: K_2SO_4 mass ratio of 1:1 were analyzed by XRD and the results are shown in Figure 5.

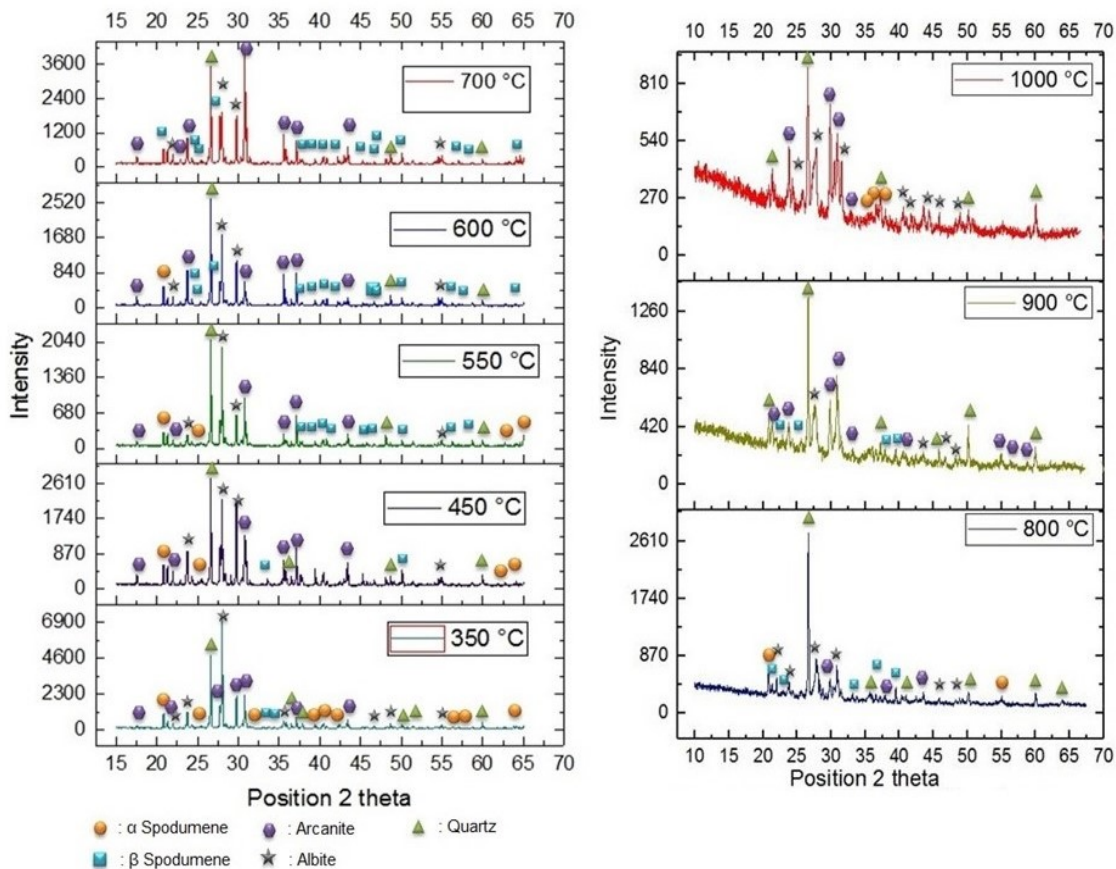
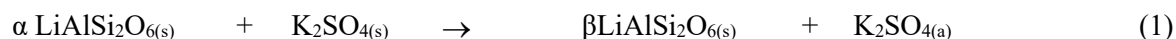


Figure 5. Diffractogram of the decomposition products with various temperatures (ore: K_2SO_4 mass ratio of 1:1, roasting time 60 min)

The XRD pattern in Figure 5 indicates that the roasting process induced the change of the structure and phase of minerals in the granitic ore sample. The spodumene minerals which is initially has alpha phase with monoclinic crystal system was transformed into beta phase with tetragonal crystal system. The change in the structure and phase starts to be detected at roasting temperature of 350 °C with 60 minutes roasting time. This β -spodumene was detected at 2 thetas of around 31° and 33.5° according to ICSD 98-001-4235. However, this phase disappeared at roasting temperature of 1000°C and roasting time of 60 minute. At this temperature, arcanite (K_2SO_4) was detected with the peak position at 2 thetas of around 31° and 33.5°. The arcanite has orthorhombic crystal according to ICSD 98-000-2827. The optimum temperature to generate β -spodumene is 700°C (roasting time 60 minute). At this condition, α -spodumene has been well converted to β -spodumene as indicated by the XRD result of decomposition product (Figure 5). Natasha et.al. also reported an optimum temperature of 700°C with 40 minute roasting time to form β -spodumene from Kebumen sekismika rock[7].

The possible reaction mechanisms between spodumene in granitic rocks with K_2SO_4 as decomposition agent are as follows: 1) alpha spodumene is converted to beta spodumene at temperatures of above 350°C 2) Beta spodumene phase reacts with K_2SO_4 to form Li_2SO_4 phase. At this stage, the potassium in potassium sulphate compound is replaced by lithium atom from spodumene to form lithium sulphate.

The chemical reactions proposed for the conversion of α -spodumene to β -spodumene is as follow:



The mechanism and the reaction steps during conversion of α -spodumene to β -spodumene is illustrated in Figure 6. Profile of Gibbs free energy and logarithmic of equilibrium constant of Reaction (2) as a function of temperature according to the data from HSC Chemistry Software is illustrated in Figure 7.

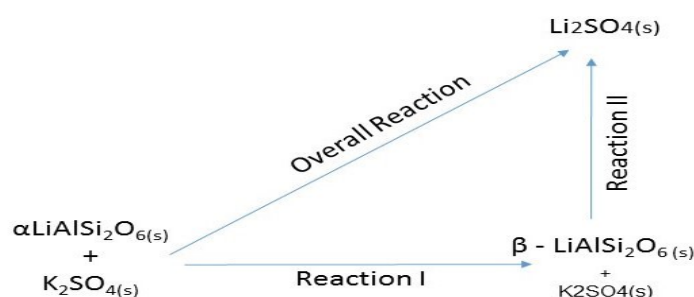


Figure 6. The mechanism reaction between α spodumene and K_2SO_4 additives.

The SEM micrographs of decomposition products resulted from roasting experiments at temperatures of 350°C and 700°C for 60 minutes are illustrated in Figure 8.a and 8.b, respectively. It was found roasting tends to reduce the grain size of the granitic ore sample. At higher roasting temperatures, smaller grain size of the decomposition product was obtained. The results of SEM analysis shows that the grain size of the decomposition product resulted from the decomposition at temperature of 350 °C is at the range of 4 – 10 μm which is notably smaller than the initial grain size of un-roasted ore which has grain size at the range of 7 - 19 μm . Further increased of roasting temperature to 700°C resulted in smaller grain size at the range of 2 – 6 μm .

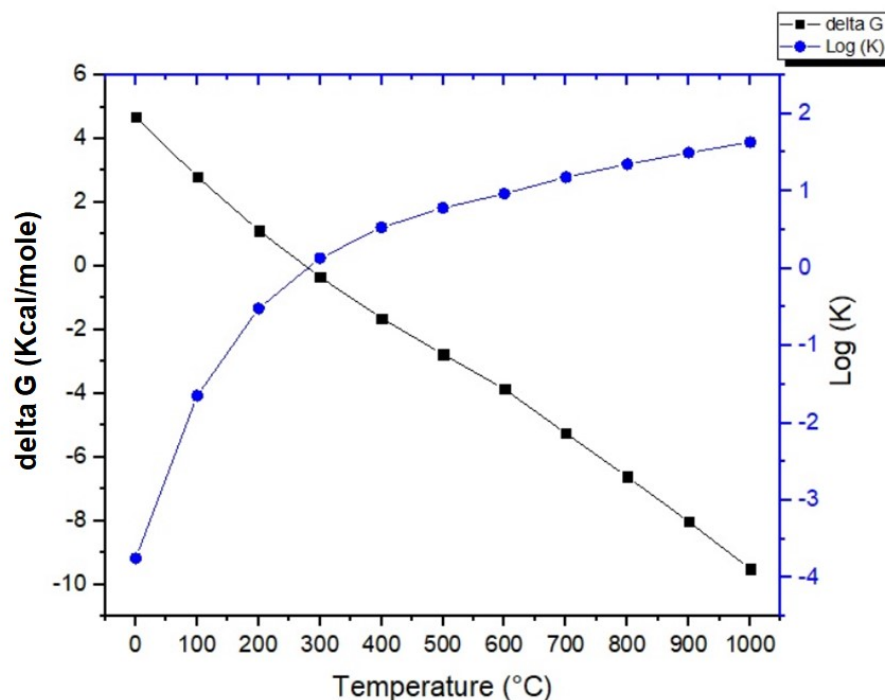
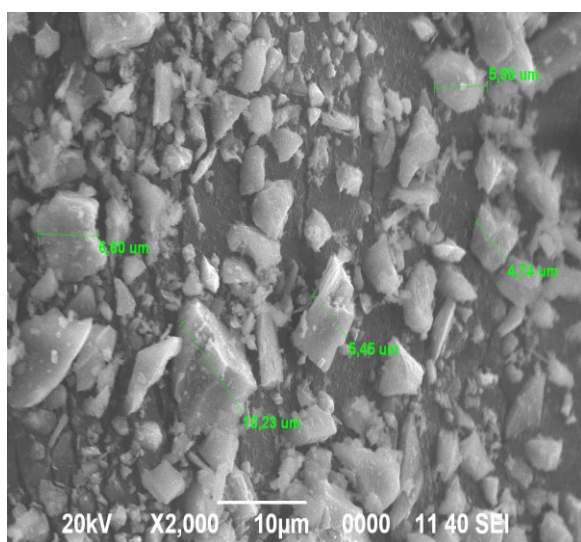
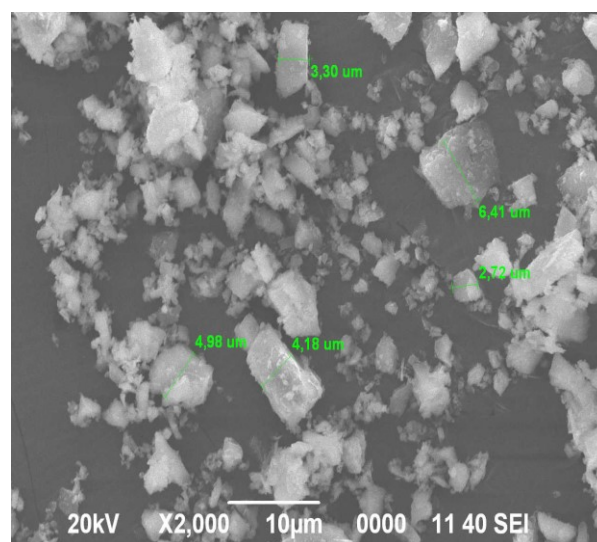


Figure 7. Profile of Gibbs free energy and logarithmic of equilibrium constant of Reaction (2) as a function of temperature according to the data from HSC Chemistry Software.



(a)



(b)

Figure 8. SEM micrographs of the decomposition products resulted from roasting experiments at temperatures of (a) 350°C and (b) 700°C for 60 minutes.

3.3 Effect of roasting time

Roasting experiments at temperature of 700°C for 20, 40 and 60 minutes were conducted to evaluate the effect of roasting times on the formation of β -spodumen-phase. XRD Diffractogram of the decomposition products resulted by roasting at temperature of 700°C 20 min, 40 min and 60 min is presented in Figure 9. The XRD pattern indicates the effect of roasting times on the formation of β -

spodumene-phase. At roasting temperature of 700°C, duration of roasting for 60 minute was found to be an optimal condition in which conversion of α -spodumene to β -spodumene took place completely. The α -spodumene began to be transformed to β -spodumene after 20 minutes of roasting at 700°C, at which β spodumene was found at peaks with 2 thetas of 22°, 23°, 26° and 33.5° according to ICSD 98-001-4235. For 40 minute roasting duration at 700°C, β spodumene was detected at peaks with 2 thetas of 22°, 23°, 26° and 33.5° according to ICSD 98-001-4235. Meanwhile for the roasting duration of 40 minute at 700°C, β spodumene was detected at peaks with 2 thetas of 22°, 23°, 26°, 33.5°, 36°, 37°, 40°, 42°, 45°, 56°, 59° and 62° according to ICSD 98-001-4235. For the roasting duration of 60 minute at 700°C, α -spodumene was completely converted to β -spodumene in which β -spodumene was detected at peaks with 2 thetas of of 21° and 47°. On the other hand, roasting duration of 20 minute and 40 minute resulted in the decomposition product which is still contains α -spodumene phase which was detected at peaks with 2 thetas of of 21° and 47° according to ICSD no. 98-001-0238.

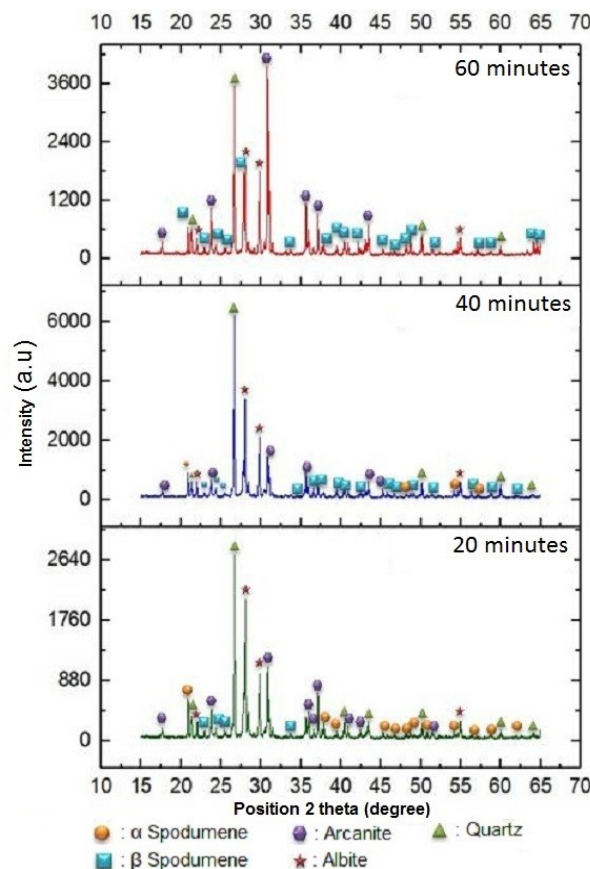


Figure 9. XRD Diffractogram of the decomposition products of the granitic ore sample at 700°C for 20 min, 40 min and 60 min

4. Conclusions

The granitic rock from South Kalimantan has major mineral components of albite ($\text{NaAlSi}_3\text{O}_8$), quartz (SiO_2) and spodumene ($\text{LiAlSi}_2\text{O}_6$). Decomposition process of the granitic ore with K_2SO_4 at temperatures of above 350°C for 60 minutes changes the crystal structure of the spodumene from monoclinic to tetragonal and its phase from α -spodumene to β -spodumene. The α -spodumene was completely converted to β -spodumene (which is more soluble in water) at roasting temperature of 700°C for 60 minute. SEM analysis of the decomposition products indicated that

roasting of the granitic ore sample reduces grain size and at higher roasting temperatures, smaller grain size of the decomposition product was obtained.

5. References

- [1]. Darman H, and Sidi F H, 2000, *An Outline of The Geology of Indonesia*, Ikatan Ahli Geologi Indonesia
- [2]. Habashi F, 1980. *Principles of Extractive Metallurgy*, **IV**. Gordon and Breach, USA.
- [3]. Helvacı C, 2003. *Int. Geol. Rev.* **45**, 1–14
- [4]. P K Choubey, M Kim, R R Srivastava, J Lee, dan J Lee, 2016 *Minerals Engineering*. **89**, 119-137
- [5]. Virginia, pp. 94 – 95 http://www.meridian-int-res.com/Projects/Lithium_Problem_2.pdf (accessed on Juli 10, 2018)
- [6]. Barbosa L I, Valente G, Orosco R P, & Gonzalez J. A. (2014). *Minerals Engineering*, **56**, 29-34
- [7]. Natashaa N C, Lalasari L H, Rohmah M, and Sudarsono J W 2018. *Majalah Metalurgi* (2018) **2**: 69 – 78.
- [8]. Peltosaari O, Tanskanen P, Heikkinen E, and Fabritius T, 2015. *Minerals Engineering*. **82**, 54-60
- [9]. N. K. Salakjani, P. Singh, dan A. N. Nikoloski, *Minerals Engineering*, **98**, 71-79, 2016
- [10]. Wang, Jianling, Wang, Jimin, Zhu, Jianchun, 1994. *Nonferrous Met.* **4** (2), 107–112
- [11]. Yan, Q., Li, X., Wang, Z., Wu, X., Wang, J., Guo, H., Hu, Q., Peng, W., 2012. *Int. J. Miner. Process*

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