A LITERATURE STUDY OF BENEFITING K-BEARING SILICATE ROCKS AS RAW MATERIALS FOR POTASSIUM FERTILIZER

STUDI LITERATUR PEMANFAATAN BATUAN SILIKAT PEMBAWA KALIUM SEBAGAI BAHAN PUPUK KALIUM

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ABSTRACT

As an agricultural country Indonesia requires NPK fertilizer up to 2.6 million tons per year. However, such a number is mostly fulfilled by imports, particularly potassium (K) fertilizer. Almost a 100% of K-fertilizer comes from Canada and Russia in the form of KCl (sylvite) salt. Indonesia does not have sylvite mineral, but retains some K-bearing minerals such as K-feldspar and leucite. Both are different in characteristics from sylvite. K-feldspar and leucite are the alumino-silicate minerals. They require special treatment to process them into K-fertilizer. Several techniques can be applied to process both minerals, such as by mechano-chemistry, leaching, alkali fusion and bioleaching. Research on the utilization of K-source minerals as a raw material for K fertilizer is relatively rare. The opportunity to conduct such a research is widely open, as currently conducted by the Research and Development Centre for Mineral and Coal Technology.

Keywords: feldspar, leucite, utilization, import, potassium fertilizer

SARI

Kebutuhan Indonesia terhadap pupuk NPK per tahun mencapai 2,8 juta ton namun pemenuhannya sebagian besar masih tergantung kepada impor terutama kalium dan fosfor. Hampir 100% pupuk berbahan dasar kalium diimpor dari Kanada dan Rusia dalam bentuk mineral silvit (KCl) sedangkan fosfor diimpor dalam bentuk batuan fosfat dari negara-negara Timur Tengah seperti Mesir dan Jordania. Indonesia sebenarnya mempunyai potensi agro-mineral yang cukup banyak untuk diolah menjadi pupuk. Permasalahannya adalah kualitas yang belum memenuhi standar seperti yang disyaratkan produsen pupuk; sebagai contoh, mineral silikat berbasis kalium seperti K-felspar dan leusit yang karakternya berbeda dengan silvit sehingga memerlukan perlakuan terlebih dahulu agar kualitasnya memenuhi standar. Beberapa teknik dalam mengolah mineral alumino-silikat adalah aktivasi mekanis, pelindian, peleburan dengan alkali dan bioleaching. Kajian mengenai pemanfaatan mineral berbasis kalium untuk pupuk memang masih jarang namun kesempatan untuk melakukan hal tersebut terbuka luas seperti yang saat ini dilakukan oleh Puslitbang Teknologi Minertal dan Batubara.

Katakunci: felspar, leusit, pemanfaatan, impor, pupuk kalium

INTRODUCTION

Along with phosphor and nitrogen, potassium is one of the essential elements as fertilizer notably for the plant growth and reproduction. The element also serves as a regulator since entering the 60-enzyme systems within the vegetation. It helps vegetation to endure the effects of temperature as well as increases plant resistance to disease. Potassium is needed, especially for carbohydrate-

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rich crops such as potatoes. Testing shows that the right amounts of potassium results in long and strong growing of cotton, increasing rind endurance, extending rose branches, strengthening and greening the grass, and increasing the size and quality of fruit, grains, and vegetables (Warmada, 2004).

In 2012, the needs of NPK fertilizer in Indonesia reached 2,593,920 tons (Ministry of Agriculture, 2012). Approximately 96% of Indonesian farmers use the fertilizers to cultivate the farm, and the rest (4%) applies organic fertilizer. Of the three component types within such as compound fertilizer, phosphate and potassium are imported. Even for potassium, a 100% belongs to import, particularly from Canada and Russia. The potassium import is around 435,000 tons / year or 61.6 million USD (Azis, 2001). The price of KCl has increased 4 times since 2007 (Manning, 2010). It reached US$1000 per ton K_2O that is equivalent for some contract during 2008. Referring to such condition, the use of crushed silicate rocks needs to be considered as an alternative for K-source. The rocks are occurs widely in the world and could be a significant role in maintaining soil fertility for the poorest farmers.

K-bearing silicate rocks contain most of the essential nutrients that plants require for growth and development. The ground silicate rocks can be used for fertilizer and potentially provides the nutrients to plants in various soil environments. When used, the fertilizer yields slow release performance. It continually improves soil and harvest quality. Its application to highly weathered, low fertility, acid soils has been proposed as an alternative to conventional fertilization with water-soluble fertilizers in areas where fertilizers are not available or in organic agriculture (van Straaten, 2002). The appliance of K-bearing silicate rocks also refers to benefiting quarry by-products as occurred in West Australia, Queensland and Brazil as part of an alternative sustainable strategy to re-mineralize or recapitalize degraded soils (Priyono in www.ntb.litbang.deptan.go.id).

Based on its rock-forming minerals, the silicate rocks are divided into mafic and felsic ones. The former is dominated by ferro-magnesian silicate minerals that perform (mostly) dark color and contain base cation such as Mg, Ca, micro nutrients of Mn, Fe, Cu and Zn with less K (< 1 % K_2O). The later is characterized by light minerals that are rich in silica (quartz and/or feldspar) but poor in nutrient content. The K content within the rocks is sufficient (4-20%). Figure 1 shows both rock types. The choice of silicate rocks for silicate fertilizer depends on type and lack intensity of the nutrients. In this case, the silicate fertilizer of feldspar and gneiss as K source is more appropriate than that of basalt and dolerite. The later belongs to mafic rocks.

Resources of these commodities in Indonesia are quite abundance, but those are generally in low

(a)

(b)

Figure 1. Basalt as one of mafic rocks that rich in micro nutrients but less in potassium (a) and a felsic rock (rhyolite), rich in silica (either quartz or feldspar) but poor in micro nutrients (Wahyudi et al., 2012)

quality. This condition results in the dependency of potassium import for this country. Figure 2 shows the demand of NPK fertilizer in Indonesia. Indonesia retains abundantly K-bearing silicate rocks; however, study regarding the use of such rocks for silicate fertilizer is very limited. Based on data from Center for Geological Resources (Kusdarto, 2008), there is a K-mineral reserves in Situbondo regency, East Java. The mineral is leucite or KAlSi2O6 and amounting to 117.5 million tonnes (inferred) and 12.5 million m3 (measured). Besides leucite, other K-mineral is feldspar that is found almost in all parts of Indonesia, especially Java and Sumatra (Mandalawanto, 1997). In addition to K- mineral resources, trachyte that spreads out in South Sulawesi is available at district Barru, Pankep, Sinjai, Soppeng and Bone. Their total reserve is 4.1 billion tons. The next source of K-mineral is biotite or (K(Mg, Fe) 3AlSi3O10 (F,OH)2). The biotite occurs at North and South Sumatras (Center for Geological Resources, 2009).

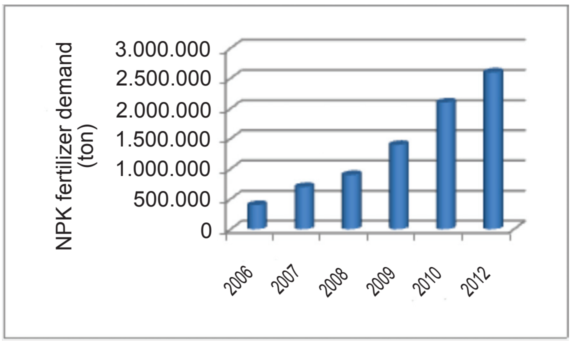


Figure 2. Demand of NPK fertilizer in Indonesia (modified from the Ministry of Agriculture, 2012)

Naturally, mineral as the source of potassium is divided into two groups, namely the salt and silicate groups as shown in Table 1. Most of fertilizer industry still uses potassium from salt groups such as sylvite since its K-level is already high (60% K_2O) and the solubility is good enough to easily absorb by plants. Unfortunately, Indonesia has no K-salt mineral similar to sylvite. The K-minerals that is commonly found in Indonesia is potassium silicate minerals but its application is still very rare due to its solubility limitation hence mineral activation is required to make it gains good solubility.

METHODOLOGY

A literature survey is a main method used for this study. The study was completed by collecting primary and secondary data either quantitative or qualitative. The data included K-bearing silicate rock resources, its mineral charcteristics and employed proces for processing the rocks to be potasssium-based fertilizer. All data were then evaluated.

RESULTS AND DISCUSSION

Carbon (C), Hydrogen (H), oxygen (O), nitrogen (N) ,phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), nickel (Ni), molybdenum (Mo) and chlorine (Cl) are the essential micro nutrients for plant growth while cobalt (Co), silicon (Su), and sodium (Na) serve as additional nutrients and required by only certain plants in certain environmental condition. Some of the various nutrients are available within silicate

Table 1. Classification of natural K-bearing minerals (modified from Warmada, 2004)

K-source			
Salt Group	Formula	Silicate Group	Formula
Sylvite	KCl	Orthoclase	$KAlSi_6O_8$
Arcanite	K_2SO_4	Sanidine	$KNaAlSi_3O_8$
Glasserite	$3K_2SO_4$ N_2SO_4	Phlogopite	$KMg_3(AlSi_3O_{10})$ $(OH)_2)$
Cainite	4KCl $4MgSO_411H_2O$	Biotite	$K(Mg,Fe)_3(AlSi_3O_{10}(OH)_2)$
Carnallite	KCl $MgCl_2$ $6H_2O$	Leucite	$KalSi_2O_6)$
Langbeinite	K_2SO_4 $2MgSO_4$	Trachyte	-
Niter	KNO_3		

rocks and are dissolved by rock-weathering agent through a bio-geochemical process. Nutrients are released and absorbed by plants that are grown on a rock-weathering soil. Weathering and dissolving process of nutrient-bearing rocks naturally occur gradually and take places much slower than that of nutrient adsorption by plants. Increasing the cropping intensity and the use of high-yielding variety that is voraciously adsorb the nutrients excessively require the nutrient supply within soil to maintain the optimum harvest. The use of the one and the only fertilizer, i.e., NPK in some places and continual deficiency of soil nutrients result in imbalance and lack of various soil nutrients as well as acidity of the soil that will finally decrease the fertilizing effectiveness. As an effort, nutrient-bearing silicate rocks combined with manure may replace the depleted nutrients within soil. However, study on silicate rock fertilizer (SRF) should be focused on the effort to accelerate nutrient solubility within soil by modifying factors that controls the SRF dissolution and evaluating the effectiveness of SRF agronomy on various vegetations and soils.

The potassium within feldspar is normally resistant to weathering process. The K+ is not easy to be released from its host. As a result, the plant retains difficulty to absorb such an ion. On the contrary; the K ion along with the Mg^{2+} and Fe^{2+} that is available in mica or micaceous clay will be easily absorbed by the plant. Mica and clay have a silicate sheet structure and the three ions are bound within the sheets. Such a feature will easily free the ions. Kusdarto in http://psdg.bgl.esdm.go.id states that the resource of K-bearing minerals in Indonesia is available only in trachytic and rhyolitic rocks as found at Mount Kunyit, Lampung but rhyolitic tuff occurs at Paga village, East Nusa Tenggara. However, the potassium at such places is employed for ceramic industries instead of fertilizer purpose. The K-bearing minerals cannot directly be used for fertilizer. It needs to be processed prior to using it, notably upgrading its K content. Another K-bearing mineral is leucite. The mineral takes place around Mount Muria, Central Java within pyroclactics, tephrite, basanite lava, leucite and syenite rocks but its resource has not yet been studied.

Research and Development Centre for Mineral and Coal Technology or known as tekMIRA has conducted several research regarding the beneficiating K-bearing silicate rocks during 2012 (Wahyudi et al., 2012). The research were focused on upgrading the K content available within the rocks. Two sample types containing K-feldspar and leucite were taken from two areas, namely Jepara and Situbondo. The K-feldspar was sampled at Mount Ragas of Jepara while leucite-bearing rocks came from Payak (Jepara) and Patemon (Situbondo). Though the minerals retain potential reserve, beneficiations of such minerals have not yet been conducted by either the local residents or private entrepreneurs. Observation during field activities shows that the K-silicate rocks are used for building materials and other construction purposes as noticed at Patemon of Situbondo (Figure 3).

Based on the presence of mineral resources in Indonesia as well as a large potassium demands within country for fertilizer, it needs a research regarding exploiting Indonesian K-mineral to be used for fertilizers. Methods that could potentially be used to process leucite and feldspar as raw materials for potassium fertilizer include mechanochemistry, alkali fusion and bioleaching. The three technologies refer to upgrade the K-content as well as its solubility but prior to processing it, the minerals need to be tested their characters both chemistry and mineralogy. XRD analyses shows that Mount Ragas K-feldspar consists of sanidine - $(K,Na)AlSi_3O_8$ while leucite-bearing andesite from both Payak and Patemon comprises leucite - $KAlSi_2O_6$, augite - $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$, anorthite $CaAl_2Si_2O_8$ and illite - $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$. Potassium oxide of Mount Ragas K-feldpar is 6.58% while leucite-bearing andesite from Payak and Patemon has respectively 11.37 and 10.32% of K_2O.

Characterizing the samples prior to processing also includes SEM-EDS analyses as well as testing the solubity of potassium in citric acid 2%. Figure 4 represents SEM-EDS analyses of Mount Ragas K-feldspar (a) and leucite-bearing andesite of Patemon (b). SEM-EDS analyses shows that one particle of Mount Ragas K-feldspar contains K_2O around 7.51% while the K_2O content within leucite of Patemon is about 22.58%. The fact that the K_2O content within Mount Ragas K-feldspar is lower than that of Patemon leucite supports the result of chemistry analyses. Of the three K-silicate samples, the most soluble K within citric acid belongs to that of Payak leucite (11.23%) while Patemon leucite keeps middle solubility (5.87%). The lowest K content pertains to Mount Ragas K-feldspar (0.24%). Due to its low solubility, the Mount Ragas K-feldspar is not proper to be

Figure 3. Bulk of leucite-bearing andesite at Patemon village of Situbondo is resided along the village road to be sold as construction materials (Wahyudi et al., 2012)

upgraded its K content for fertilizer but Patemon leucite along with Payak leucite is still prospective to be processed for K fertilizer by upgrading the material through several methods (Wahyudi et al., 2012).

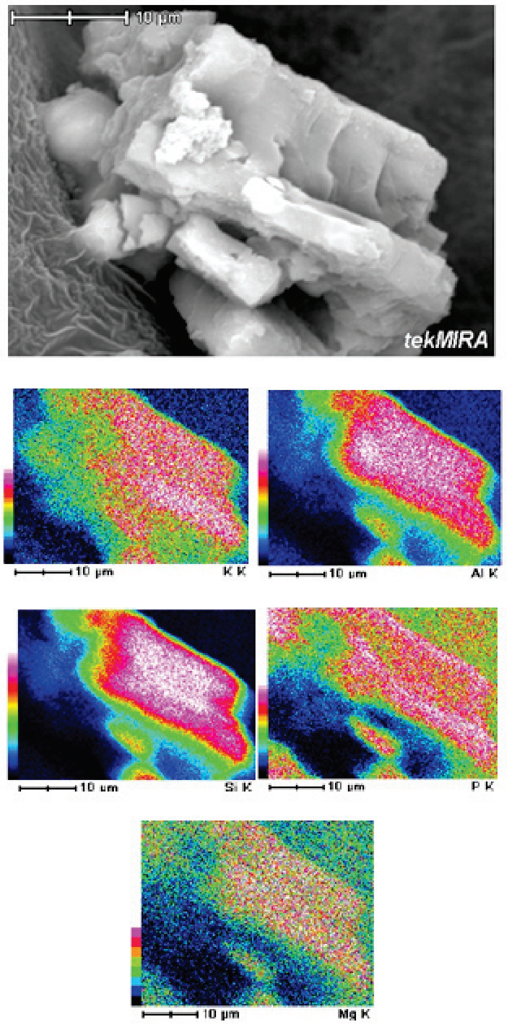
The following are some methods that could potentially be used to process leucite and feldspar as raw materials for potassium fertilizer. Those are mechano-chemistry, alkali fusion and bioleaching.

Mechano-chemistry

Mechano-chemistry is a technology that addresses the changes in chemical and physical properties of the particles due to mechanical energy; for example is a continuous grinding process. Such a treatment will provide reactive particles and make them easier for further processing such as extraction process (Alacova, 2004). Kleiv (2007) had conducted mechanical activation in terms of processing K-feldspar. Material used in this project was the mill products. Methods for characterizing the material included size distributions, specific surface areas and their relative degree of structural disordering as calculated from X-ray diffraction analysis. Figure 5 shows the XRD pattern for K- feldspar after milling process that results in damaging mineral structure. From the XRD point of view, it was clear that less than 10 minute milling was sufficient to make the K-feldspar mineral more reactive. This pre-treatment will facilitate the next process, namely extracting potassium element from its host. The change of surface properties in the lead cation K-feldspar make it easily released into the soil, hence it can be absorbed by plants.

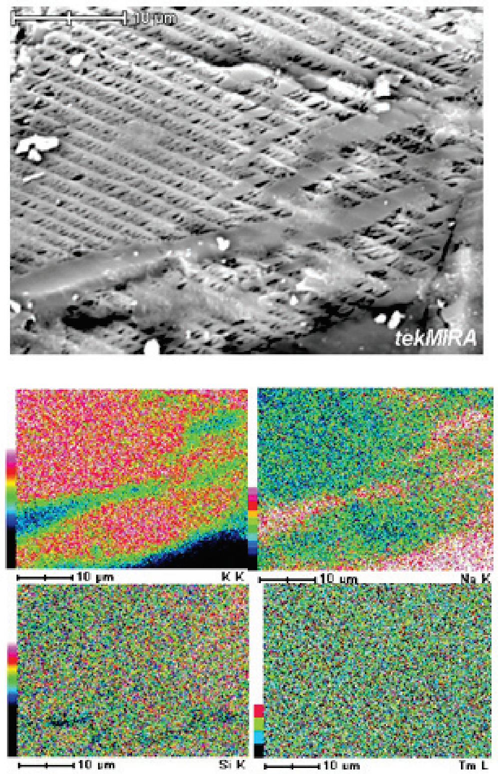
Alkali Fusion

Alkali fusion is a process that is often used for separating certain elements within silicate compounds, such as separating zirconia from its sili-



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		49.29							
Mg K	1.253	0.39	1.30	1.14	MgO	0.64	0.12	0.3212	
Al K	1.486	11.89	1.25	15.75	Al2O3	22.47	3.43	12.6852	
Si K	1.739	28.94	1.36	73.66	SiO2	61.92	8.03	30.5062	
P K	2.013	3.25	2.20	3.75	P2O5	7.45	0.82	4.0023	
K K	3.312	6.24	0.96	5.70	K2O	7.51	1.24	9.8752	
V K									
Bi M									
Total		100.00		100.00		100.00	13.65		

(a)



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		41.55							
Na K	1.041	9.33	1.42	13.35	Na2O	12.57	3.75	7.5048	
Si K	1.739	30.23	1.04	70.85	SiO2	64.68	9.95	26.5200	
K K	3.312	18.74	0.78	15.77	K2O	22.58	4.43	23.1615	
Tm L	7.175	0.15	4.54	0.03	Tm2O3	0.17	0.01	0.1571	
Total		100.00		100.00		100.00	18.14		

(b)

Figure 4. SEM-EDS analyses of Mount Ragas K-feldspar (a) and Patemon leucite (b). The former provides K2O content lesser than that of the later (Wahyudi et al., 2012)

cate (Yamagata, 2010). Yuexin (2009) employed the method to separate potassium from silicate minerals. The process was carried out by mixing K-silicate minerals with alkali (such as NaOH, $CaCO_3$, etc.) at certain temperature and time normally around 600 ^{0}C for 2 hours. The results are then leached with water and then filtered to separate the potassium-containing residue and Na-silicate-bearing filtrate. The residue is then re-purified to obtain a high K_2O content. The

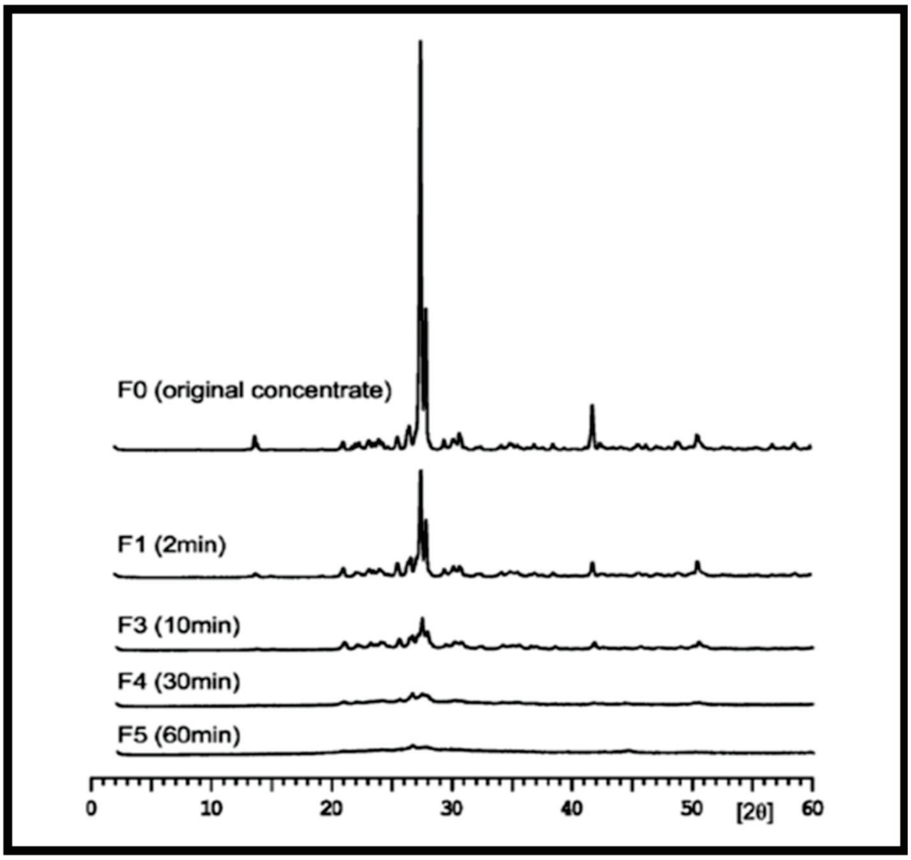


Figure 5. XRD patterns of K-feldspar curve after activation by means of advanced mechanical milling (modified from Kleiv, 2007)

flow chart of the alkali fusion process is shown in Figure 6.

A number of K-silicate mineral was roasted at 200 to 700 ^{0}C for 0,5 to 3 hours. The products were then dissolved by water in room temperature and stirred in a magnetic stirrer for 30 minutes. Separating the solid and liquid employed Buchner funnel as illustrated in Figure 7. The solid products were then tested their K solubility in 2% citric acid.

Bioleaching

Bioleaching is an alternative process to extract potassium due to its cheap cost production and environmentally friendly (Maochun et al., 2002). The process can employ various microorganisms such as bacteria and fungi. The microorganisms, attached to mineral surface, create micro-environments in which the ligand concentration, acidity and redox activity can be increased substantially compared to its initial state thus affecting the mineral exchange reactions. Bacteria, fungi and other plants also produce compounds that can interact with the mineral surfaces to dissolve certain elements (Badr, 2006).

Of the various microorganisms that can be used for bioleaching, *Aspergillus niger* and *Penicillium expansum* – the fungi – are among them. The former is included within Ascomycetes class and Aspergillaceae family and are easily found in almost organic materials (Wolf dan Wolf, 1997) and the later belongs to Eurotiomycetes class and Trichocomaceae. When grown, they produce an organic acid compound, namely oxalic acid as a by-product from citric acid fermentation. As a leaching agent, the compound can dissolve heavy metals from bauxite, kaolin, nepheline, quartz sand, tailing mud and spodumene (Ubaldin et al., 1996; Gorbushina, 2006). Factors affecting oxalic acid production include carbon source and pH condition. Study on K-extraction from leucite mineral using *Penicillium expansum* and *Aspergillus niger* shows that around 21% to 27% potassium

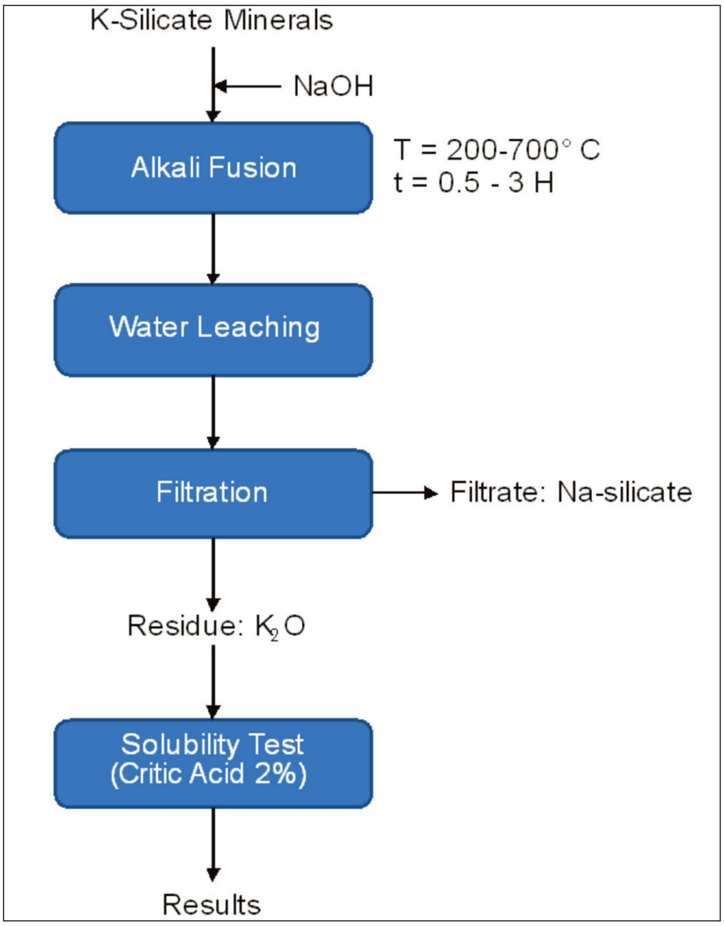


Figure 6. A flow chart regarding alkali fusion for processing K-silicate minerals (modified from Yamagata, 2010)

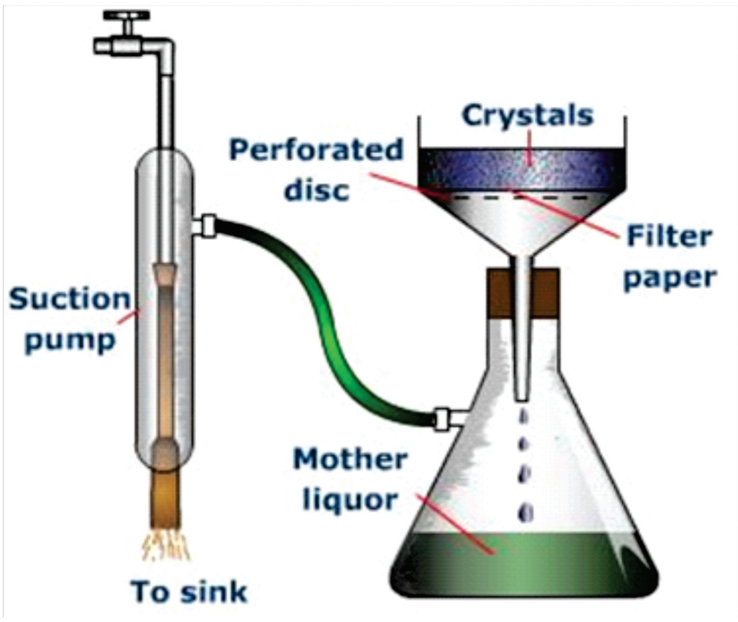


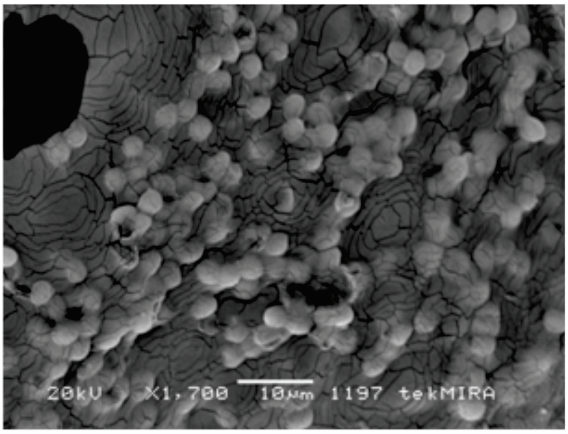
Figure 7. A diagram of solid – liquid separation using Buchner funnel (modified from http://www.umich.edu/~chemh215)

were successfully recovered by microbial leaching (van Straaten, 2002). This phenomenon indicates that the fungi ability is good enough to extract potassium from silicate rocks. Figure 8 shows both micro-fungi in the growth state.

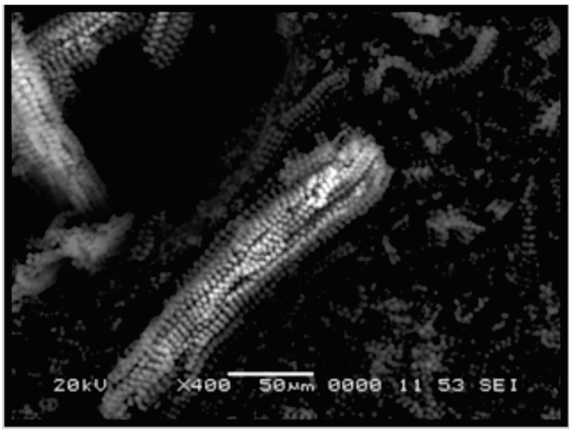
The choice of process to beneficiate K-bearing silicate rocks depends on several factors. One of them is the characteristics of processed sample. Economical and environmental aspects are also factors to be considered prior to selecting such methods. Others are shown in Table 2.

CONCLUSIONS

K-bearing silicate rocks contain essential nutrients for plants that in a long term will effectively affect soil characters and harvesting results. This will ensure production sustainability with less negative impacts to the environment. The efficiency of K-bearing silicate rocks may be increased through high energy milling, however, such a method needs intensively studied both technical and economical aspects. A combination of manure and K-bearing silicate rocks can serve as natural fertilizer for replacing chemical one. Indonesia retains raw materials of either manure or K-bearing silicate rocks sufficiently. However, study regarding the use of K-bearing silicate rocks for fertilizer making is very limited. *tek*MIRA has studied feldspar and leucite beneficiations since 2010 as raw materials for K-fertilizers. The research is still ongoing until today. The technologies mentioned above are expected to increase the K-solubility and thus fit to be used for fertilizer. Thus, in turns, it will lessen Indonesian potassium imports as well as serve as a provider to fulfill national fertilizer demand.



(a)



(b)

Figure 8. Microorganisms that can be used for extracting potassium from K-silicate minerals; (a) Penicillium expansum and (b) Aspergillus niger (Handayani,et al., 2008)

Table 2. Characteristics of mechano-chemistry, alkali fusion and bioleaching – the three processes to beneficiate K-bearing silicate rock for K-based fertilizer

Considered factors	Method		
	Mechano-chemistry	Alkali fusion	Bioleaching
Instrument	advanced mill	furnace/kiln	reactor
Reagent/media	-	chemical (NaOH)	micro-organism (fungi)
Energy consumption	High	high	low
Process duration	Intermediate	fast	slow, time-consuming
Process	Simple	complicated	simple and cheap
Environmental aspect	not friendly, requiring safetyaction to handle nano size product is required	not friendly, producing a tailings	friendly

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