EFFECT OF REAGENT VOLUME AND CONCENTRATION ON RECOVERIES OF MgO AND SO$_3$ WITHIN SYNTHETIC DOLOMITE-BASED KIESERITE

PENGARUH VOLUME DAN KONSENTRASI REAGEN TERHADAP KANDUNGAN MgO DAN SO$_3$ DALAM KISERIT SINTETIS BERBAHAN DASAR DOLOMIT

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ABSTRACT

Natural kieserite is usually used for the production of epsom salt and fertilizer. Normally, the mineral is mined from geologic marine deposits and provides a soluble source of both Mg and S for plant nutrition. However, natural kieserite cannot be found in Indonesia. The fact that this country retains a lot of dolomite deposits and such a material can be processed into synthetic kieserite by sulphatization process seems promising for fertilizer industry in Indonesia. Varying the sulfuric acid concentration between 2 and 5 N and its volume from 29.50 to 94.80 ml produces the MgO in MgSO$_4$ filtrate below the specification as stated in Indonesian National Standard (14 – 19%) though its sulfur content has satisfied the requirements. It is assumed that some MgO's (around 1.93 – 7.12%) are still available in CaSO$_4$ deposit. To get the optimum results, an appropriate calculation is required when adding sulfuric acid to the process and the solution should be in neutral condition prior to separating MgSO$_4$ – CaSO$_4$ as well.

Keywords: kieserite, dolomite, sulfuric acid, MgO, MgSO$_4$, CaSO$_4$

SARI

Kiserit alam umumnya digunakan untuk pembuatan garam epsom dan pupuk. Mineral ini kaya akan magnesium (Mg) dan belerang (S)sebagai nutrisi tanaman dan biasanya diperoleh dari endapan marin. Kiserit alam tidak ditemukan di Indonesia namun negeri ini mempunyai endapan dolomit yang melimpah dan dapat diolah menjadi kiserit sintetis dengan proses sulfatasi, nampaknya menjanjikan bagi industri pupuk di Indonesia. Memvariasikan konsentrasi asam sulfat antara 2 dan 5N serta volumenya antara 29.50 -94.80 ml menghasilkan MgO dalam filtrat MgSO$_4$ yang nilainya di bawah spesifikasi yang disyaratkan Standar Nasional Indonesia (SNI) yaitu sebesar 14 – 19% walaupun kandungan belerangnya sudah memenuhi persyaratan SNI. Rendahnya MgO dalam filtrat diduga karena sebagian dari oksida tersebut (sekitar 1,93 – 7,12%) terbawa endapan CaSO$_4$, oleh karena itu untuk memperoleh hasil optimum diperlukan perhitungan konsentrasi dan volume yang tepat ketika menambahkan asam sulfat ke dalam proses, selain itu larutan harus dalam kondisi netral sebelum pemisahan MgSO$_4$ – CaSO$_4$.

Kata kunci: kiserit, dolomit, asam sulfat, MgO, MgSO$_4$, CaSO$_4$

INTRODUCTION

A highly unstable magnesium sulfate mineral, kieserite ($MgSO_4$ H_2O), was first identified by Reichardt of Strassfurt, Germany in 1860. It is named after Dietrich Georg von Kieser who died in 1862 in terms of honoring his dedication in physics and science. In nature, kieserite has a vitreous luster and shows colorless, grayish white or yellowish appearance. Retaining hardness of 3.5, the mineral performs monoclinic crystal system. Natural kieserite is commonly found at countries with four seasons such as Germany, Great Britain and so on. The availability of the mineral is not yet known in Indonesia although as an agricultural country, the country requires this mineral for fertilizing palm and other plantation crops. Yet the mineral can synthetically be made through a series chemical reaction by reacting dolomite mineral with sulfuric acid (Singh, 2013).

Dolomite, $CaMg (CO_3)_2$, is relatively abundance in Indonesia. The mineral is available in East Java and South Sumatera (http://www.dolomite.co.nz/page/2/, Badan Penelitian dan Pengembangan Propinsi Sumatera Utara, 2009). It shows a double bond of carbonate compound to Ca and Mg elements and hold hardness of 3.5 – 4 Moh's scale as well as density of 2.85. As a non metal material, dolomite is used for refractory, cement, flux and fertilizer industries. Its usage for fertilizer will have added value if processed to kieserite that retains slow release property. Research on kieserite making had been conducted by Atangsaputra (2000), Agung and Wahyudi (2008), Wahyudi and Agung (2010). The former used serpentinite as raw material, however, its process was relatively cost-consuming due to roasting requirement in its procedure. The second research is also relatively expensive as its procedure is relatively complex. Dolomite as raw material was calcined to be CaO and MgO. Water addition to the products or known as slaking process will get $Ca(OH)_2$ and $Mg(OH)_2$. If both products are reacted with sulfuric acid, it will produce soluble magnesium sulfate and insoluble calcium sulfate. The product can be separated through filtration process. Precipitating

the soluble product will get synthetic kieserite. The process in the third research is relatively simple. No sea water addition in its procedure.

The objective of this study is to evaluate extraction performance of magnesium from domestic dolomite using sulfuric acid. The study uses dolomite from Sedayu-Gresik, East Java. However, prerequisite for synthetic kieserite making requires dolomite that has MgO and CaO contents around 20 and 30% respectively. Chemical analysis on Sedayu dolomite shows that the material owns MgO and CaO contents around 21.6 and 30.3% respectively. Its LOI is 47.5 (Table 1). Kaczmarek and Sibley (2011) states that if the MgO content within dolomite between 20.5 – 21.9%, such a material belongs to the high-Mg dolomite and will be excellent for kieserite making. However, relatively high CaO content (30.3%) will affect sulfuric acid addition. Other element contents are normally small hence its effect can be ignored.

METHODOLOGY

Prior to conducting the leaching, dolomite as raw material needs to be prepared using jaw crusher and ring mill to get -150-mesh dolomite particles for experiment feed and raw material characterization. The characterization includes chemical, XRD, XRF and SEM-EDS analyses as well. Started by calcining the feed in a furnace at 900°C, the process will change dolomite into its oxides, namely CaO and MgO while the carbonate (CO_3) is released to the air as CO_2. The water is then added to the yielded material in terms of changing them into hydroxide materials, namely $Ca(OH)_2$ and $Mg(OH)_2$. Sulfuric acid addition with certain concentration and volume to such hydroxides will perform $CaSO_4$-$MgSO_4$ suspension. Separating the mixture using filter paper no. 40 – a standard filter paper, splits $CaSO_4$ lump and $MgSO_4$ filtrate. The purpose of this step is to produce $MgSO_4$.xH_2O compound. Such a compound is produced by precipitating the filtrate at 200°C - a standard temperature for precipitating the crystal water from $MgSO_4$ salt. Precipitation time depends on

Table 1.   Chemical analysis of Sedayu dolomite

Tested material	Content (%)									
	MgO	CaO	LOI	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	TiO_2	P_2O_5
Dolomite	21.6	30.3	47.5	0.10	0.15	0.079	0.006	0.027	0.029	0.091

quantity volume and no other material addition during filtrate precipitation.

The x is expected to be equal to 1 in order to the MgO and sulfur contents are appropriate with natural kieserite mineral. Figure 1 shows the flow chart for kieserite making.

RESULTS AND DISCUSSION

A series leaching experiment for kieserite making was conducted at laboratory scale by varying the volume and concentration of sulfuric acid. Such a variation was required in terms of understanding its effect on the derived MgO and SO_3 concentra-
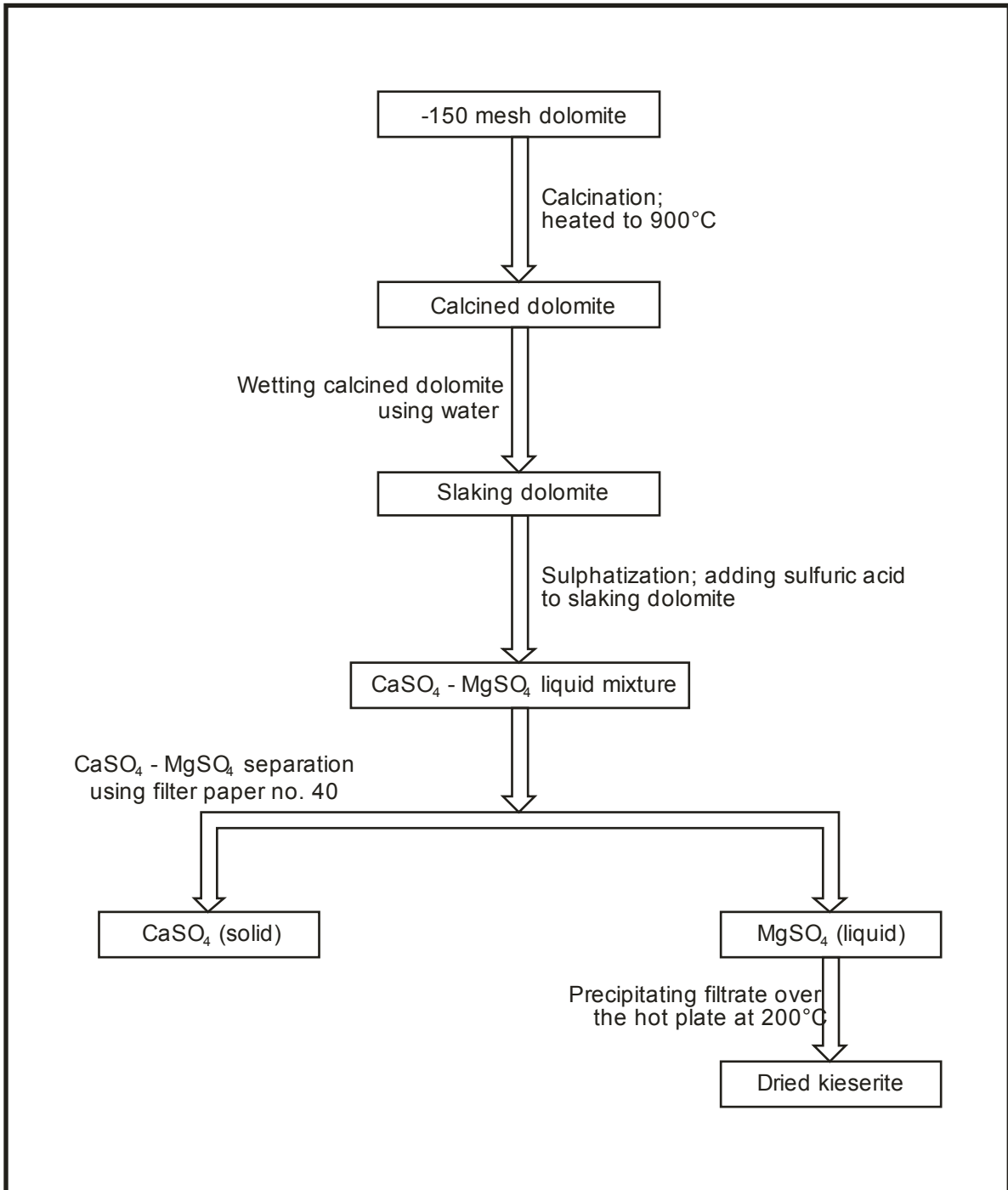
Figure 1. A flow chart for kieserite making

tions. The leaching was accomplished in a 1-liter leaching tank as shown in Figure 2. Reactions occur within tank are as follows:
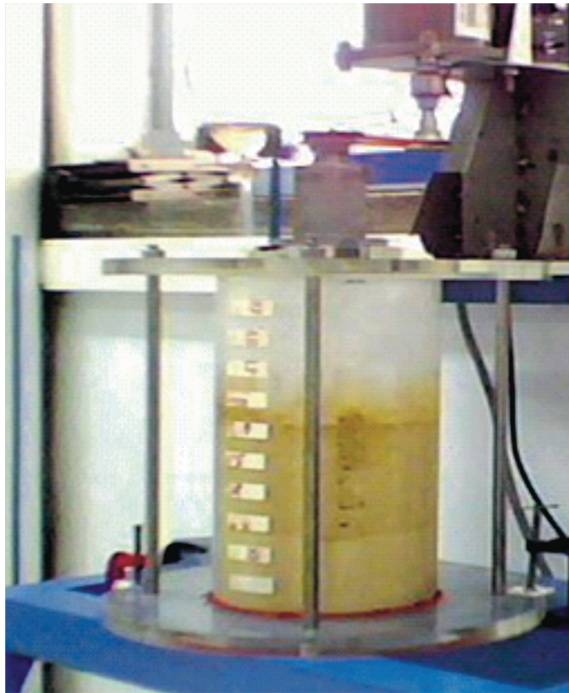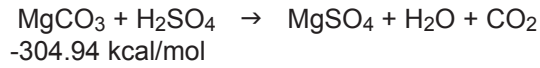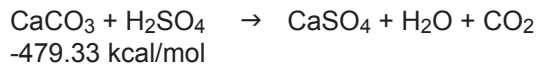
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$
-479.33 kcal/mol

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$
-304.94 kcal/mol

Figure 2.   A leaching tank for kieserite making

$CaSO_4$ retains solubility of 5.16 x 10-6 g/100 ml while the $MgSO_4$ solubility is around 25.5 g/100ml. The former owns solubility lesser than that of the later.

Table 2 shows the effect of sulfuric acid addition on kieserite making. The data were derived by analyzing suspension material (after reacting dolomite with sulfuric acid) without precipitation process. This means that the kieserite has not yet been defined. It is shown that the more sulfuric acid added, the bigger yielded $MgSO_4$. As a result, the MgO from each experiment performs varying content. When reacted with material A, concentration and volume of H_2SO_4 are 2 N and 73.8 ml respectively. Compared to material C, such a concentration is lesser 2.5 times but its volume is 2.5 times bigger. Theoretically, the $MgSO_4$ filtrate occurs from the experiments should provide similar MgO concentration for both material with testing code A and C. Similar phenomenon occurs to materials with testing code B and D. Differences in MgO concentration for those materials are supposed to occurs due to some MgO's are still entrapped in $CaSO_4$ deposit. To convince such an assumption, it requires a series of tests to analyze the MgO within $CaSO_4$ deposit. The test results are shown in Table 3 that shows differences in MgO concentration for materials with testing code A, B, C, D and E. Such differences are supposed to be occurred due to the effect of $MgSO_4 – CaSO_4$ filtering process as the amount of filtered MgO within $MgSO_4$ filtrate is different with the amount of MgO within $CaSO_4$. If the MgO from Table 2 is combined with similar

Table 2.   Effect of sulfuric acid addition to kieserite making based on reagent volume and concentration

Testing code	Dolomite quantity (g)	Concentration of	Volume of	MgO	SO3
		H_2SO_4		quantity	
		(N)	(ml)	(%)	
A	10	2	73.80	14.46	28.60
B	10	2	94.80	16.67	33.00
C	10	5	29.50	14.72	29.20
D	10	5	37.90	17.92	35.60
E	10	5	45.01	19.65	38.00

Note: the data were taken by analyzing suspension material after reacting dolomite with sulfuric acid.
        Precipitation process was not conducted.

material from Table 3, it provides the amount that is relatively related to Table 1. For example, combining the MgO content of testing code A in Table 2 (14.46%) with similar material of testing code A in Table 3 (7.12%) will present 21.58%. Such a figure is relatively close to the MgO content of raw material (21.60%) as presented in Table 1. Similar circumstances occur to the sum of MgO materials for testing code B, C, D and E in both Table 2 and 3 that provide quantity relatively near the MgO content of raw material. Yet, in terms of getting optimum result, appropriate calculation is required when adding sulfuric acid to the process and the solution should be in neutral condition prior to separating $MgSO_4$ – $CaSO_4$ as well. Filtering solution, conducted in acid or excessive acid conditions, will result in damaging the instrument for accommodating both $MgSO_4$ filtrate and $CaSO_4$ deposit. As a result, reagent wasting as well as time and cost consuming occur.

Table 3.   MgO concentration within CaSO4 deposit

Testing code	Concentration of MgO in CaSO$_4$ (%)
A	7.12
B	4.88
C	6.85
D	3.63
E	1.93

Other experiments were conducted to evaluate time for making kieserite. Precipitating $MgSO_4$ filtrate will yield dried-synthetic kieserite that has formula $MgSO_4.xH_2O$. Yet the 13-hour precipitation time is not a standard. Such a figure is required to precipitate all $MgSO_4.xH_2O$ within filtrate. Yet all experiments employ the optimum condition derived from previous experiments (Table 2). The product is then analyzed for the MgO and sulfur contents (Table 4). Indonesian National Standard (INS) states that the minimum MgO and S contents in kieserite should be at least 25.5 and 21% respectively (Table 5). Referring to such a standard, all experiments have satisfied the provision. However, its moisture has not yet known as the equipment for moisture testing is unavailable. Two more tests were conducted in terms of evaluating the time of kieserite formation. Condition for the tests referred to condition of testing code DD in Table 4 but the precipitation time

was reduced to 8 and 5 hours in terms of saving the time although the produced kieserite is not as white and dry as previous one. DD condition is selected due to its highest MgO content and neutral pH. Yet the EE condition is not chosen due to its acid condition. Table 6 illustrates the results. Of both experiments, only testing code FF satisfies the IIS standard for both MgO and sulfur contents. Another test provides result that is out of the IIS requirement. However, either MgO or sulfur contents in testing code FF are lesser than that in testing code DD. It is assumed that both tests require longer precipitation time to perform complete kieserite material and material in testing code FF belongs to initial kieserite formation, not yet fully grown kieserite. Another material occurs during kieserite formation is $MgSO_4.6H_2O$ as shown in Figure 6. To confirm such a presumption, a series of XRD test was conducted to standard kieserite, material from testing code DD, FF and GG. The results are shown in Figure 3 through 6. Spectra of material from testing code DD and FF present similar performance with spectrum of standard kieserite though their intensities are quite different. Standard kieserite shows intensity of its spectrum around 2000 (Figure 3) while materials from testing code DD and FF own intensities of 1500 and 1400 respectively (Figure 4 and 5). The difference in intensity of both materials means that there is dissimilarity in kieserite

Table 4.   MgO, SO$_3$ and S contents in kieserite products for each experiment.

Testing code	Precipitation time at 200°C	Concentration of		
		MgO	SO$_3$	S
	(hrs.)	(%)		
AA	13	27.1	53.7	21.4
BB	13	27.0	53.5	21.4
CC	13	26.7	53.0	21.2
DD	13	27.4	54.4	21.8
EE	13	27.5	54.6	21.8

Table 5.   Requirements for kieserite fertilizer (source: http: pustan.bpkimi.kemenperin. go.id/files/SNI%2002-2807-1992.PDF)

MgO	S	Moisture
	contents (%)	
min. 25.5	min. 21.0	max. 0.5

Table 6.   Confirmation tests for evaluating kieserite formation.

Testing code	Precipitating time at 200°C	Concentration of H_2SO_4	Volume of	Concentration of		
				MgO	SO_3	S
	(hrs.)	(N)	(ml)	(%)		
FF	8	5	37.9	26.4	52.4	21.0
GG	5	5	37.9	24.3	48.6	19.4
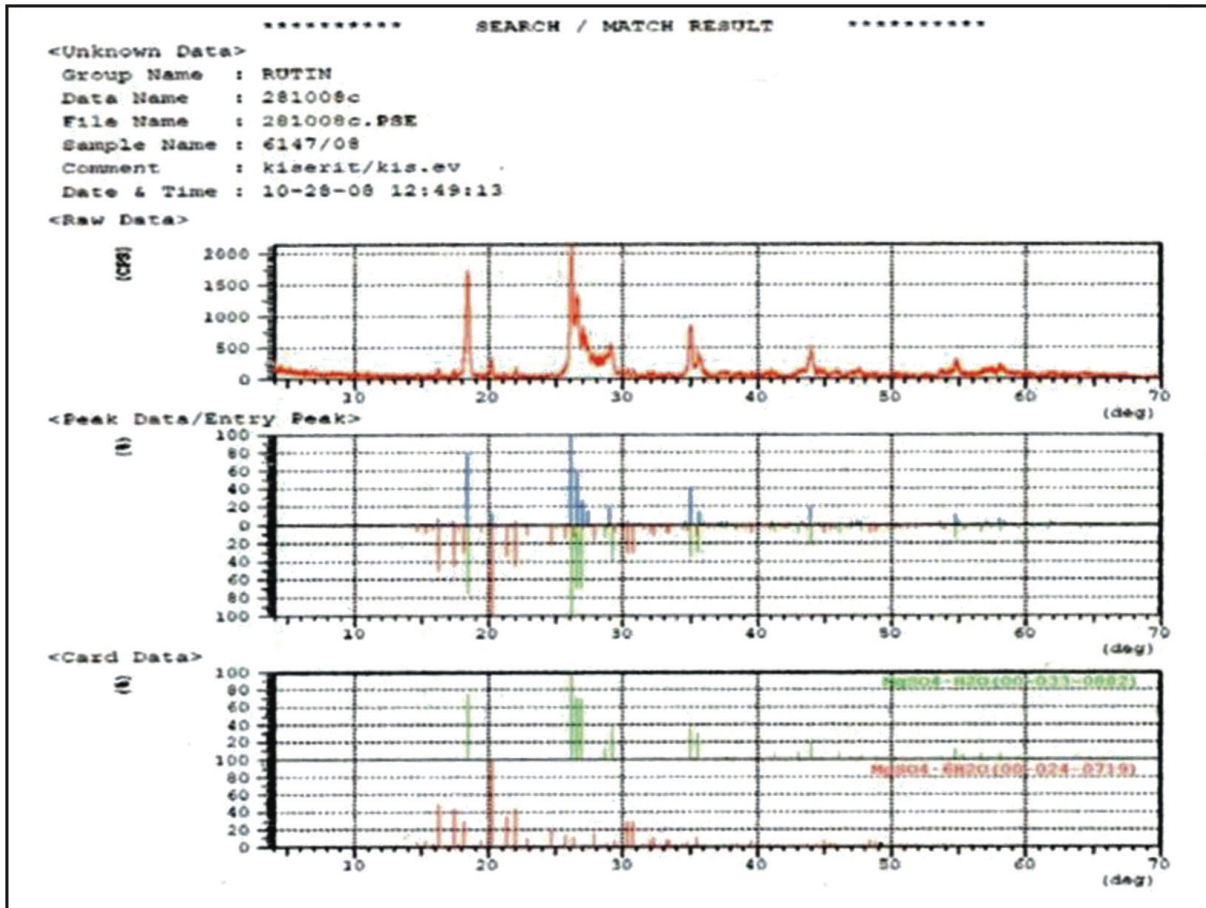
Figure 3.   Kieserite standard detected by XRD showing intensity of 2000

quantity of both materials (http://www.geology.wmich.edu/koretsky /mineralogy/14xrd.pdf). It is presumed that the length of precipitation time as the cause; the longer the precipitation time, the higher the intensity. Material from testing code GG illustrates differences in both performance and intensity (Figure 6). It means the kieserite has not yet been established. The red line in Figure 3 refers to $MgSO_4.6H_2O$ or standard kieserite while the green lines in Figure 4 and 5 belong to $MgSO_4.H_2O$. This means that the XRD analyses espouse the chemical analyses. Such MgO and sulfur contents in material DD and FF has satisfied pre-requisite to be kieserite mineral although both of them are categorized as the initial stage of kieserite development. XRF analysis was conducted only to material labeled as testing code D to identify macro- and micro elements available within the material. The choice of material D to be analyzed refers to consideration that such a material is a representation of synthetic kieserite.
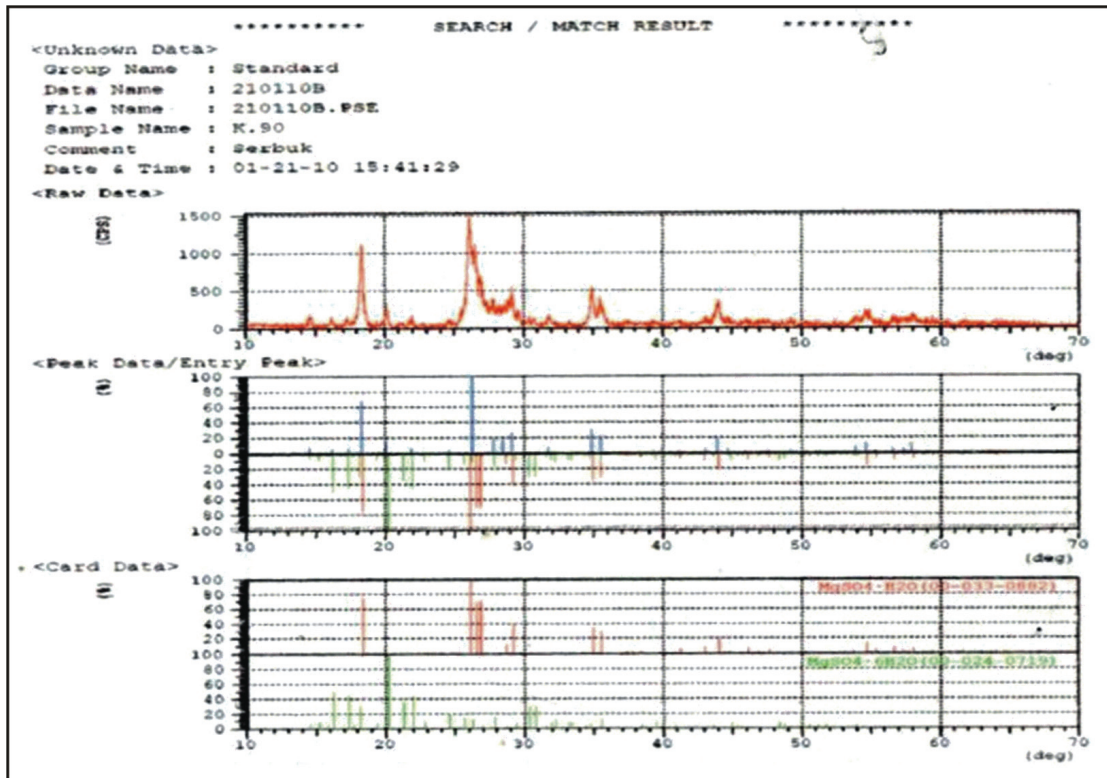
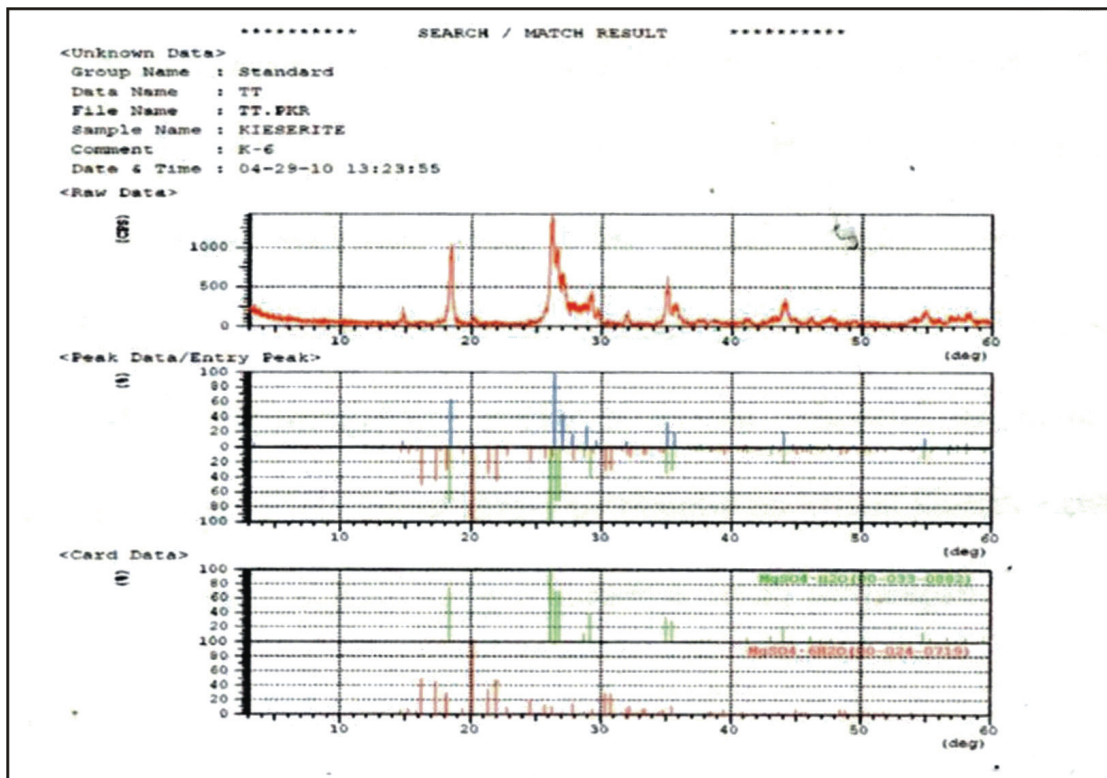Figure 4.   Kieserite from testing code D detected by XRD showing intensity of 1500

Figure 5.   Kieserite from testing code F detected by XRD showing intensity of 1500

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*********  SEARCH / MATCH RESULT  *********
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 Data Name   : 210110
 File Name   : 210110.PSE
 Sample Name : Kieserit
 Comment     : Serbuk
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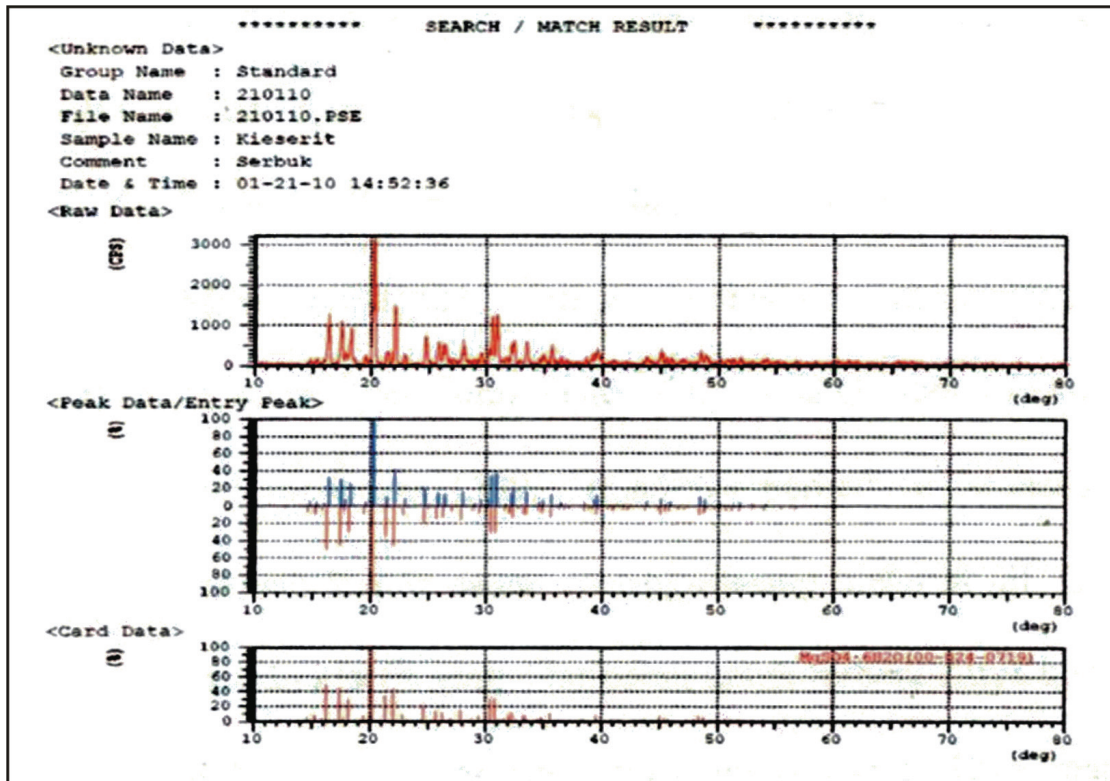
Figure 6.   Kieserite from testing code G detected by XRD showing different spectra from either Figure 3, 4 or 5

Figure 7 illustrates XRF analysis results of material DD – a material that comes from dried filtrate. There are three sharp peaks that embody magnesium (Mg), silicon (Si) and sulfur (S). The three of them belongs to macro elements, however, the Si element does not come from tested material. Its existence occurs as a material addition due to few quantity of the material. Si serves as a base in order to get a flat surface of the tested material. The fact that Mg and S are detected means that the material is kieserite although its formation is in initial stage (Ma et al., 2009).

A series of experiment was conducted to verify at what condition the kieserite formed. Constraints used in the experiments include time and temperature as either variable or fixed parameters. The first experiment employed sulfuric acid, water volume and temperature as fixed factors. The sulfuric acid was set to 5N, the water volume to 40 ml and temperature to 200°C. The result is shown in Table 7a. It is revealed that at hour 1 and 1.5, the kieserite has not yet been developed and starts growing at hour 2. The crystallization water or calculated H_2O within kieserite formula turn out to be small. It seems that the longer

precipitation time the lesser the amount of crystallization water. When the precipitation time was set to the fixed one (8 hours), sulfuric acid and water volume to 5N and 40 ml respectively; the temperature for kieserite making varies from 150 to 190°C. Table 7b illustrates the result; at 150 and 160°C, the kieserite has not yet defined. The calculated crystallization water relates to 2.7 and 2.3 respectively. Similar to Table 7a, it seems that the bigger the precipitation temperature the smaller the crystallization water.

The fact that temperature and time affect calculated crystallization water can also be confirmed by SEM photomicrograph (Figure 8). The figure shows that at hour 1 no more crack takes place (Figure 8a). The calculated H_2O is 6.7 and the mineral surface is relatively dense. More cracks occur at hour 2 (Figure 8b). Its calculated crystallization water is around 1.8. During this time, kieserite starts developing. At hour 5 and 15, the mineral looks dry and its calculated crystallization water is 1.2 and 1.1 respectively. The fact that temperature and time affect calculated crystallization water can also be confirmed by SEM photomicrograph (Figure 8). The figure shows
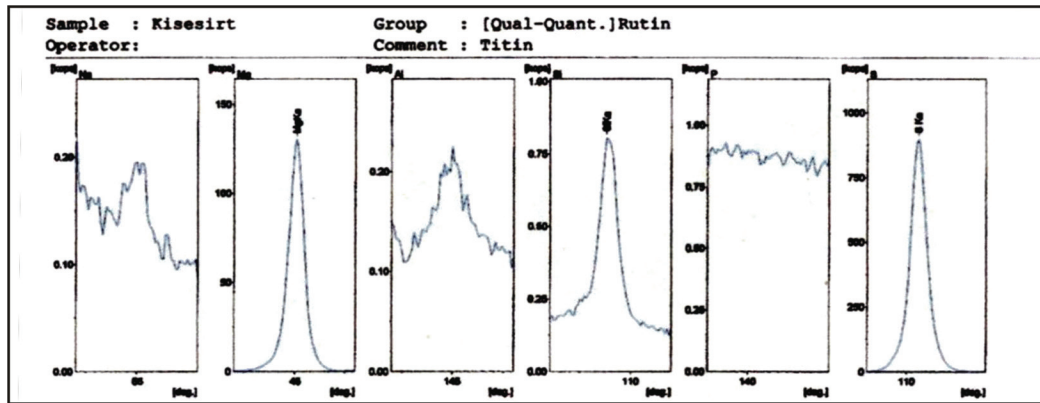
Figure 7. XRF analysis of material DD showing the available elements within the tested material

Table 7. Calculated crystallization water, MgO, SO3 and S for synthetic kieserite

a. Fixed temperature (200°C)

Variable time (hrs.)	Calculated H$_2$O	MgO content (%)	SO$_3$ content (%)	S content (%)	MgSO$_4$ formula	Kieserite formation
1.0	6.7	16.83	33.5	13.4	MgSO$_4$. 6.7H$_2$O	not yet defined
1.5	6.5	16.99	33.9	13.5	MgSO$_4$. 6.5H$_2$O	not yet defined
2.0	1.8	26.50	52.8	21.1	MgSO$_4$. 1.8 H$_2$O	defined
2.5	1.5	27.50	54.8	21.9	MgSO$_4$. 1.5H$_2$O	defined
3.0	1.3	28.30	56.3	22.5	MgSO$_4$. 1.2H$_2$O	defined
5.0	1.2	28.50	56.8	22.7	MgSO$_4$. 1.2H$_2$O	defined
10.0	1.2	28.50	56.8	22.7	MgSO$_4$. 1.2H$_2$O	defined
15.0	1.1	28.70	57.3	22.9	MgSO$_4$. 1.1H$_2$O	defined
20.0	1.1	28.70	57.5	23.0	MgSO$_4$. 1.1H$_2$O	defined
25.0	1.1	28.70	57.5	23.0	MgSO$_4$. 1.1H$_2$O	defined

b. Fixed time (8 hours)

Variable temp. (°C)	Calculated H$_2$O	MgO content (%)	SO$_3$ content (%)	S content (%)	MgSO$_4$ formula	Kieserite formation
150	2.7	23.8	47,8	19,12	MgSO$_4$. 2.7H$_2$O	not yet defined
160	2.3	24.8	49,6	19,84	MgSO$_4$. 2.3H$_2$O	not yet defined
170	1.8	26.4	52,7	21,1	MgSO$_4$. 1.8H$_2$O	defined
180	1.7	26.6	53,5	21,4	MgSO$_4$. 1.7H$_2$O	defined
190	1.3	28.0	56,2	22,5	MgSO$_4$. 1.3H$_2$O	defined

that at hour 1 no more crack takes place (Figure 8a). The calculated H$_2$O is 6.7 and the mineral surface is relatively dense. More cracks occur at hour 2 (Figure 8b). The calculated crystallization water for Hour 2 is around 1.8. During this time, kieserite starts developing. At hour 5 and 15, the mineral looks dry and its calculated crystallization water is 1.2 and 1.1 respectively.
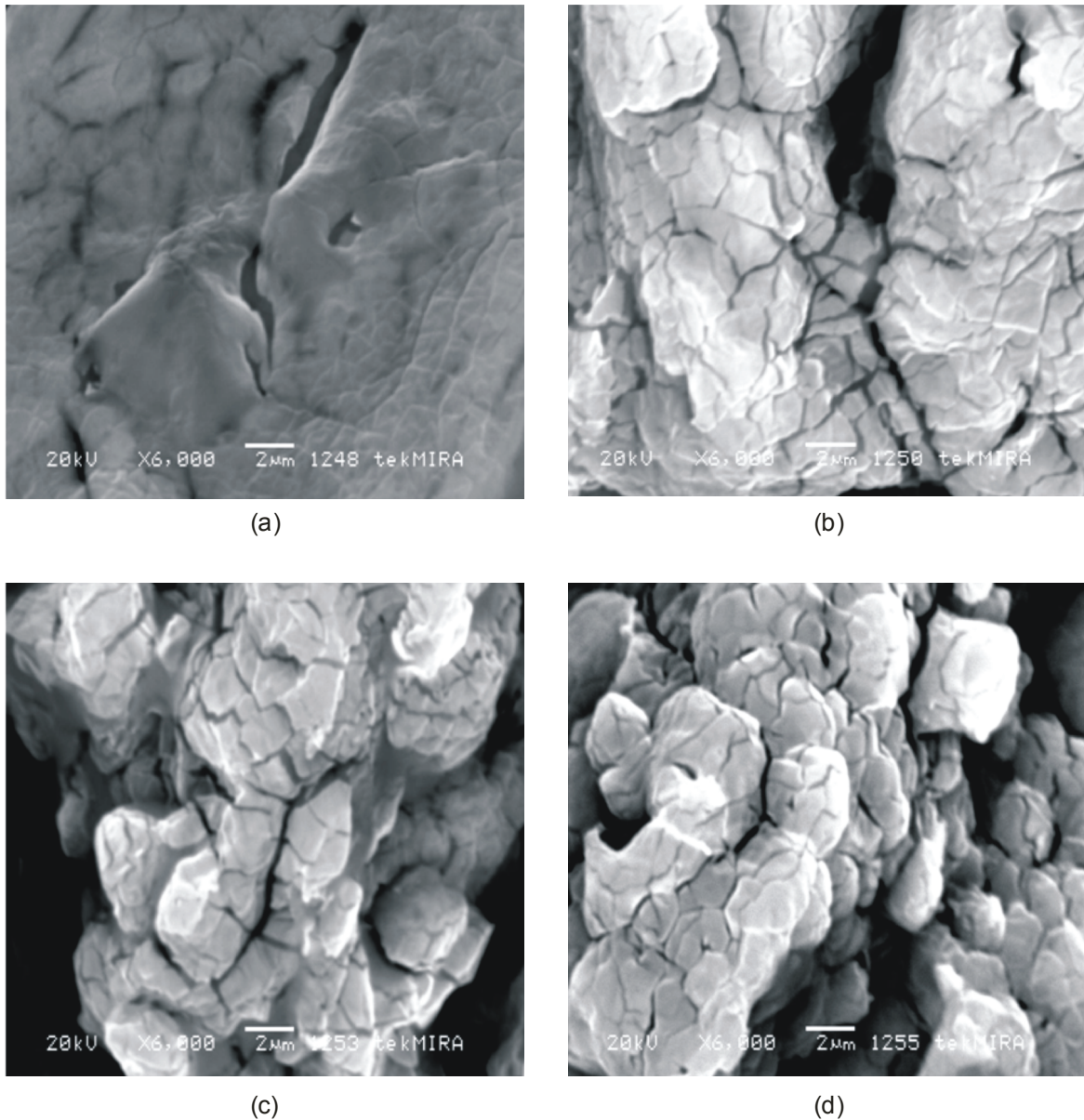
(a)

(b)

(c)

(d)

Figure 8.   SEM photomicrograph for synthetic kieserite showing relative moist kieserite at 1-hour precipitation time (a), relative dry at 2-hour kieserite development (b) and dry at 5- and 15-hour growth (c and d)

If the crystallization water develops into smaller number, on the contrary the MgO, SO_3 and S contents seems to develop as illustrated in Figure 9. The former portrays the content of synthetic kieserite component at fixed temperature. It is clear that kieserite starts growing at hour 2 and all components seems to increase from such a time until the end of the process. Referring to the IIS, either MgO or S contents has satisfied the require-ments but its moisture is over the pre-requisite that requires 0.5 % as a desired maximum content.

CONCLUSIONS

MgO contents within $MgSO_4$ filtrate are lesser than that in Indonesian National Standard. The standard requires that minimum MgO should be 25.5% but derived MgO varies from 14.46 to 19.65. It seems that the acid concentration and its volume for conducting the experiments should be increased. Some MgO's are supposed to go to $CaSO_4$ deposit as confirmed by several tests.

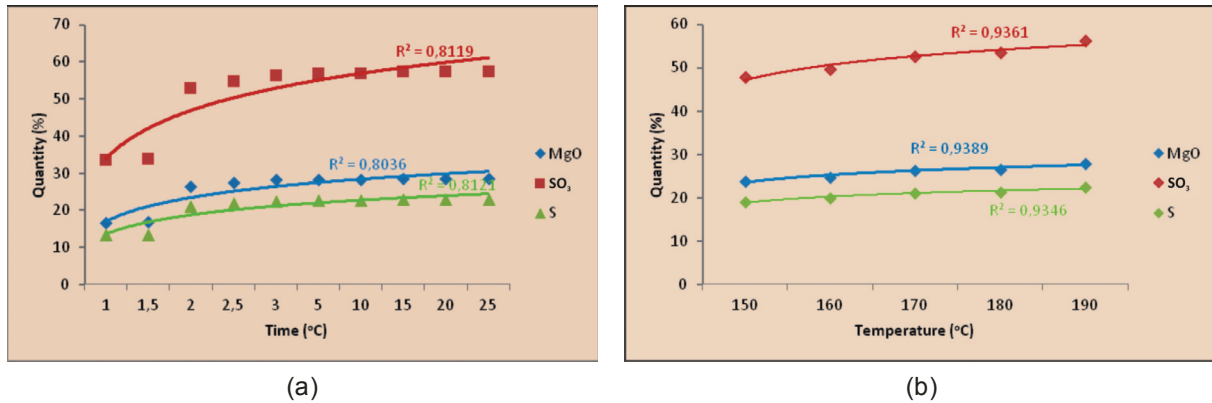(a)   (b)

Figure 8.   Quantity of kieserite components

Precipitating $MgSO_4$ filtrates at 200°C for 13 hours obtains dried kieserite. The MgO and sulfur contents satisfies INS requirement. The yielded MgO's in 5 experiments (testing code AA through EE) vary from 26.7 to 27.5%. Its S contents also meet with the IIS requirement. It ranges from 21.2 to 21.8%. Confirmation test regarding time for kieserite formation shows that 8 hours relate to kieserite development. The XRD test also verifies that material with labeled as testing code D belongs to the initial stage of kieserite formation.

The longer the precipitation time the dryer the kieserite. It seems that crystallization water is near to 1 or the formula of synthetic kieserite turn into the real one, namely $MgSO_4.H_2O$. However, it is suggested trying other experiments by varying the sulfuric acid concentration and volumes different from the previous ones.

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