STIRRING AND NON-STIRRING METHODS USED TO MAKE SYNTHETIC DOLOMITE-BASED EPSOM SALT

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ABSTRACT

The increasing need of magnesium sulfate heptahidrat by various industries and the limited availability of this material in nature are two reasons to produce $MgSO_4.7H_2O$ synthetically. Basically, such a material can be produced from dolomite. A laboratory scale of dolomite-based epsomite making which employed two crystallization processes was conducted. Those were stirring and non-stirring methods and the results showed that stirring one yielded 98.2312 to 98.7244 % $MgSO_4.7H_2O$ salt. The non-stirring method produced salts of 97.5929 – 99.0378%. Yet prior to salt processing, magnesium sulfate solution was evaporated at 100 – 110°C to get solution densities around 1.35, 1.38 and 1.4 g/ml. The bigger the density the bigger the MgO and SO_3 contents

1. INTRODUCTION

Known by its commercial name - epsom salt, epsomite is a mineral that performs a compound of magnesium sulfate heptahydrate ($MgSO_4.7H_2O$). A water-soluble bitter-tasting compound that occurs as white or colorless needle-shaped crystals was first prepared from the waters of mineral springs at Epsom, England. It also occurs as the epsomite mineral. Natural epsomite most commonly forms as efflorescence on cave walls from deposition of material from saline springs. It exists only in arid regions and in dry caves which protect it from rain and moisture, for otherwise it dissolves. Epsomite may also be formed efflorescence in tunnels of sulfide mines from the deposition of sulfur and magnesium-rich water which is created through mining operations. However, the availability of epsomite in nature is limited.

Epsom salts is used medicinally as a purgative and is also used in leather tanning, mordant dyeing, and as filler in cotton goods and paper. Needed by various industries, demand on such a substance increases from year to year (Anon., 1970; Halsey, 1974; Kirk-Othmer, 1995; Oss, 1968). Restricted natural epsom salt and increase market demand is a problem for epsom salt industry. It needs an effort to fulfill market demand. Synthetically, the material can be made from other magnesium sulfate sources. In the laboratory, dissolving magnesium, magnesium hydroxide, magnesium carbonate and/or magnesium oxide into thin sulfuric acid solution produces the salt (Halsey, 1974; Kirk-Othmer, 1995; Partington, 1957; Soin and Wilson, 1963). Yet, a large-scale epsomite making employs commercially kieserite material or known as $MgSO_4.H_2O$ (Figure1). Kieserite is less soluble in cold water. Heating such a material will change it into its anhydrate form and when the solution reaches its saturation point, cooling process bears epsomite crystal (Soin and Wilson, 1963; Taylor, 1960).

Another alternative to get magnesium sulfate heptahydrate is dissolving dolomite mineral or CaMg $(CO_3)_2$ into water-diluted sulfuric acid. The process provides magnesium sulfate solution and gypsum deposits which then are separated (Agung et al., 2000). Evaporating the filtrate followed by crystallization process at low temperature accrues magnesium sulfate heptahydrate. Dolomite is relative abundance in Indonesia and not yet benefited optimally. Referring to such a condition, emplo ying Indonesian dolomite for epsomite making will pro-

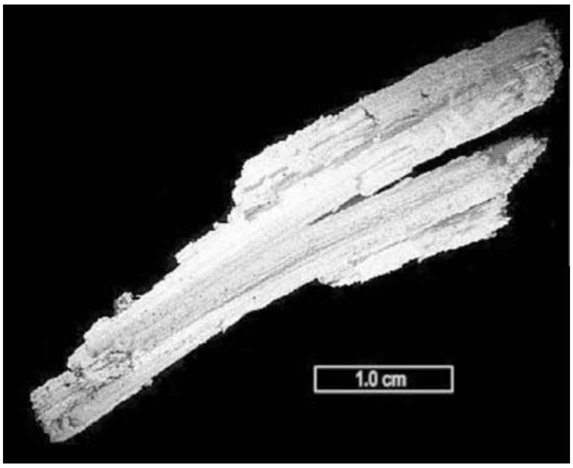

Figure 1. Natural epsomite showing pure white compact fibrous mass as its specific character (source: Weissman, webpage in webmineral.com)

vide benefit to this country; besides accomplishing the domestic need of epsomite, it is very likely Indonesia will be epsomite exporting country.

Research on epsom salt making from dolomite has been conducted at Research and Development Center for Mineral and Coal Technology. The objective of this laboratory scale research is seeking the alternative process for epsom salt making that can provide a good quality and competitive product in the market.

2. MATERIALS AND METHODS

Magnesium sulfate solution, extracted from East Java dolomite (Sedayu area), was employed as the test feed for epsom salt making. Several materials used in this study included several solutions such as HCl, HNO_3, $BaCl_2$ 10 %, NH_4OH, buffer for pH 10, EDTA and tri-ethanolamine. Other materials were KOH pellet, EBT and calcon 1% indicators and ice cube. Glass devices and supporting gadgets for this study were described in Figure 2.

Raw material and product characterization employed quantitative chemistry analysis using atomic absorption spectroscopy (AAS). Characterization was stressed on micro-and macro-contents available within raw material and product. The study also used scanning electron microscopy test to analyzed micrographic condition of synthetic kieserite that resulted from dolomite extraction to be compared with natural kieserite micrographic condition. Such a material was used as the experimental feed. Filtration, evaporation and crystallization (both stirring and non-stirring methods) were methods used in epsom salt making.

3. EXPERIMENTAL DESIGN

Started with dolomite sampling from Sedayu area in East Java, dissolving the substance into water-diluted sulfuric acid is the first step in making synthetic epsomite. The process bears magnesium

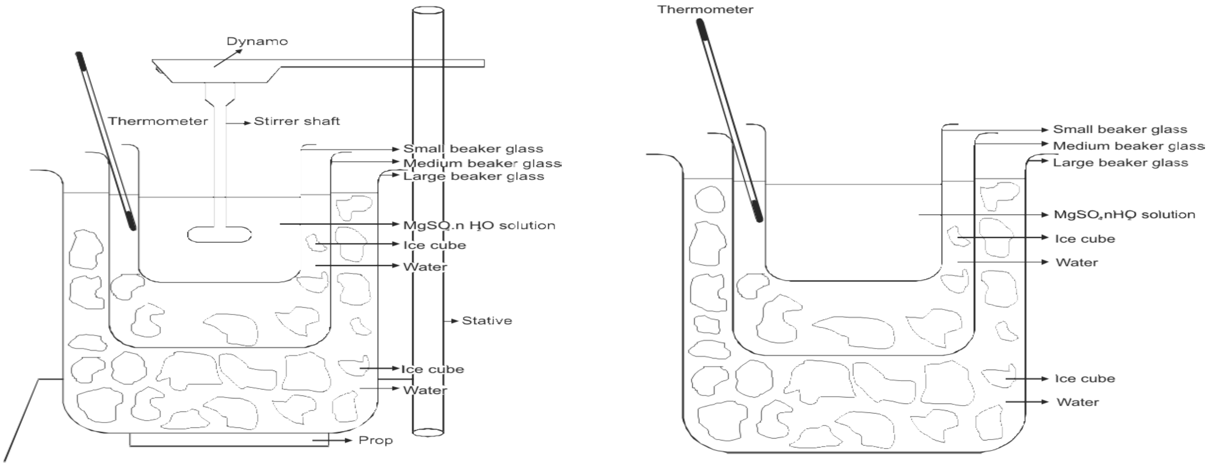

Figure 2. Glass devices and gadgets used for experiment in epsomite making using stirring (left) and non-stirring (right) methods

sulfate solution and gypsum deposit. After conducting solid-solution separation process, several treatments including filtration, evaporation and crystallization are conducted to the separated solution. Those procedures are required in terms getting the desired synthetic epsomite. Figure 3 illustrates briefly the experimental design used in this project.

4. RESULTS AND DISCUSSION

The making of epsom salt synthetic is an effort to answer the scarcity of natural epsomite as well as satisfy the increase market demand. In addition, benefiting the abundant Indonesian dolomite as synthetic epsomite source will provide added value to such a material. Yet prior to processing the material, it needs raw material study. Information derived from material characterization help anticipate any arisen problems occur during the process. In terms of anticipating whether the products have satisfied market specifications or not, it also needs conducting characterization on the products yielded from the experiment.

Raw material characterization on dolomite included determination of MgO, CaO and SO_3 contents. The results show that CaO content is the least among two other oxides (MgO and SO_3). Only 0.18% CaO is available within the analyzed raw material. The detected MgO and SO_3 are around 5.2 and 15.11% respectively. Not only were oxide contents analyzed but the iron (Fe) and dolomite density were also determined. Result shows that detected iron within sample is around 285 ppm. Referring to density determination, dolomite as raw material for kieserite making retains density of 1.24 g/cc.

Making the epsom salt required several steps (Figure 3). Dolomite was first extracted and then changed into kieserite phase by diluting the substance with sulfuric acid. Magnesium sulfate so-

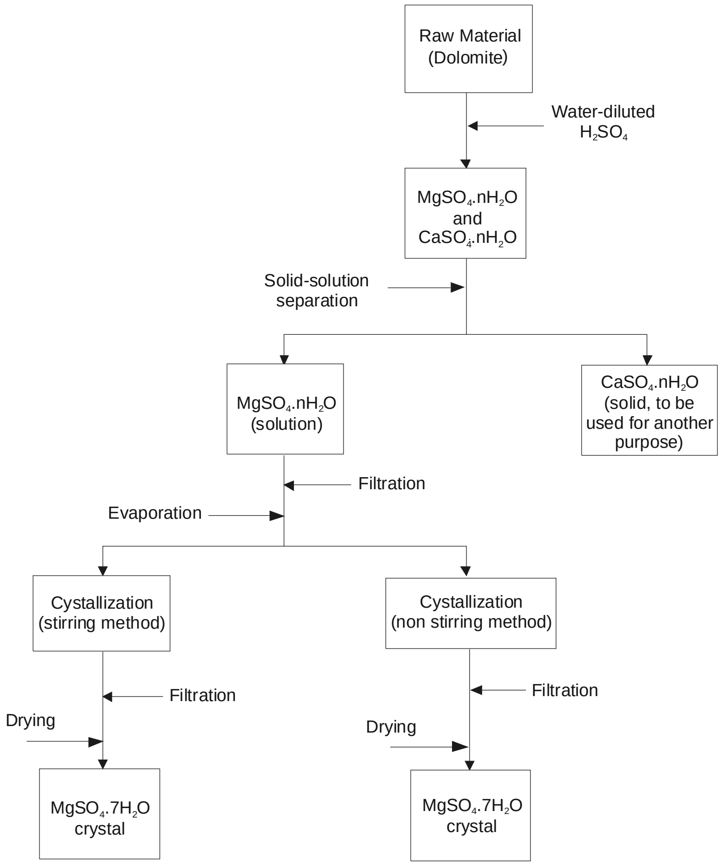

Figure 3. A flow chart illustrating experimental design for synthetic epsomite making

lution and calcium sulfate deposit occurred which were then separated. One more filtration was required to get impurity-free solution. The solution was then evaporated at 100 - 110°C. During evaporation process, water within solution diminished and resulted in thicker solution. The process could be terminated when the desired density parameter for epsomite making, namely 1.35, 1.38 and 1.40 g/cc was achieved (measured by Baume hygrometer). Prior evaporation process, solution density was 1.24 g/cc. The final step, when making epsomite, was crystallizing the solution using either stirring or non-stirring methods. Stirring rate for stirring method was determined around 124.22 rpm – the best rpm based on preliminary tests.

When evaporation process started, a small amount of $MgSO_4.6H_2O$ crystals occurred. The culprit was temperature condition during the process. Temperature of 48.2 - 67° C was a favorable condition for $MgSO_4.6H_2O$ crystallization while the epsomite ($MgSO_4.7H_2O$) crystal occurred at 15 to 48° C. Changing the process from evaporation condition to crystallization one did not immediately decrease temperature from 100 - 110° C to 15, 20 or 27° C – the desired temperatures used in this laboratory scale-research. It took more or less 45 to 60 minutes prior to reaching such temperatures. The $MgSO_4.6H_2O$ and $MgSO_4.7H_2O$ crystals which were formed before reaching desired crystallization temperature took place only on the surface of magnesium sulfate solution. This was an advantage as separating both crystals was quite easy. When reaching the desired temperature, crystallization only produced $MgSO_4.7H_2O$ crystals. Filtering followed by drying was conducted to separate the crystals from its filtrate. In terms of driving away the excess of filtrate on crystal-contai ning filter paper, a drying process was conducted by putting the filter paper on the scrap paper and left at room temperature.

Tests using stirring and non-stirring methods show that the rate of epsomite crystallization from the former method is relatively faster than that from the later method. When the process was started, epsomite crystallization occurred after 5 to 15 seconds. The crystallization initially took place surrounding stirrer which then disseminated to all media. Started at the bottom part of the media, First $MgSO_4.7H_2O$ crystallization by non-stirring method occurred a longer time, around 2 – 3 minutes after starting the process. The process was completed when all crystals filled the vessel. Not only does stirring process affect rate of crystallization but also solution density speeds up crystal formation. Non-stirring method crystallization proved these phenomena. Compared to both parameters, temperature seems less significant in influencing formation of $MgSO_4.7H_2O$ crystals. A series of tests using three different temperatures (15, 20 and 27° C) provided relatively similar product quantity for both stirring and non-stirring methods (Table 1). All crystallization process lasted for ± 30 minutes.

Analyses show that the bigger the density solution used as the feed the bigger the MgO and SO_3 contents and the lesser H_2O content. This phenomenon occurs as bigger density magnesium sulfate results in lessening H_2O concentration. The magnesium sulfate itself becomes thicker and thicker. Correlation between solution density and the contents of MgO, SO_3, H_2O from either stirring-method or non-stirring-method $MgSO_4.7H_2O$ crystals at each crystallization temperatures is shown in Figure 4.

Although uneven increase of MgO, SO_3 and H_2O contents slightly occurred, low or high crystallization temperatures did not affect those substance contents immediately. In some cases, the contents went up and then went down though the temperatures increased. It was observed that stirring method provided relatively even magnesium sulfate heptahydrate contents while those came from non-stirring method performs varying contents.

Crystallization process using stirring method yields epsom salts that are relatively stable in content, i.e., 98.23 – 98.73 %. The product variably contains MgO, SO_3 and H_2O, namely 16.23 - 16.31%, 32.07 - 32.41 %, and 48.98 - 50.46 % respectively. It is assumed that stirring process kept thick magnesium sulfate solution in homogeny condition. Range of yielded products for each conducted process is relatively the same, i.e., 0.5%.

Different from stirring-method crystallization process, the process by non-stirring method produces products that vary in content from 97.54 - 99.03 %. Its MgO content ranges from 15.68 - 16.21 %, while the SO_3 and H_2O contents are 31.16 - 32.12 % and 49.31 -50.89 % respectively. Stagnant condition of feed solution is supposed to be the culprit why magnesium sulfate heptahydrate recovery varies. During the process, formation of epsom salt molecules in every solution part is not ho-

Table 1. Characters of yielded $MgSO_4.7H_2O$ crystals including its MgO, SO_3 and H_2O contents - non-stirring method

Test no.	Temp. (°C)	Density (g/cc)	MgO (%)	SO_3 (%)	H_2O (%)	Fe (ppm)	$MgSO_4.7H_2O$ (%)
1	15	1.35	15.68	31.16	50.70	91.00	97.54
2	15	1.38	16.10	na	50.64	na	na
3	15	1.40	16.21	31.85	49.97	na	98.03
4	20	1.35	16.16	31.98	50.89	na	99.03
5	20	1.38	16.17	na	50.68	3.50	na
6	20	1.40	16.16	32.10	49.98	154.70	98.24
7	27	1.35	16.10	31.97	50.31	na	98.38
8	27	1.38	16.10	na	49.63	na	na
9	27	1.40	16.16	32.12	49.31	na	97.59

Note: na = not available

- stirring method

Test no.	Temp. (°C)	Density (g/cc)	MgO (%)	SO_3 (%)	H_2O (%)	Fe (ppm)	$MgSO_4.7H_2O$ (%)
1	15	1.35	16.23	32.07	50.40	35.00	98.70
2	15	1.38	16.30	na	50.46	4.20	na
3	15	1.40	16.30	32.38	49.70	na	98.38
4	20	1.35	16.23	32.26	50.24	na	98.73
5	20	1.38	16.30	na	50.33	57.00	na
6	20	1.40	16.31	32.41	49.52	na	98.24
7	27	1.35	16.23	32.24	50.08	na	98.55
8	27	1.38	16.31	na	48.98	14.70	na
9	27	1.40	16.31	32.41	49.51	6.30	98.23

Note: na = not available

mogeny. Though range of yielded products is big enough (1.49%), epsom salt recoveries from non-stirring method are relatively significant. Both stirring and non-stirring method products perform relatively small iron contents from 3.5 to 154.7 mg/l. Significant decrease occurs in Fe contents if compared to the Fe content within raw materials (285 mg/l).

Physically, magnesium sulfate heptahydrate crystal yielded from stirring method performs fine grain size (powder). It is very likely that propeller mechanical movement – when used for mixing solution - inhibited the crystal growth. Different from stirring method product, the product from non-stirring method shows needle-like performance. The crystals grew as feed solution was relatively stagnant.

Crystallizing magnesium sulfate solution that retains density of 1.35 g/cc at 15 and 27ºC produces $MgSO_4.7H_2O$ crystals. Figure 5 shows that the epsomite crystal derived from the tests is quite similar to that of natural epsomite as shown in Figure 1. The crystal performs relatively fibrous character as owned naturally by the epsom salt though the fibrous character of synthetic epsomite is not as perfect as that of the natural one. This might be occurred due to condition for synthetic crystal formation in laboratory is quite not the same as that for the natural epsomite in the nature. Yet in terms of convincing that the produced crystals are really epsom salt, both type of products were then analyzed by XRD. Information from XRD analysis suggests that the yielded products belong to $MgSO_4.7H_2O$ as shown in Figure 6.

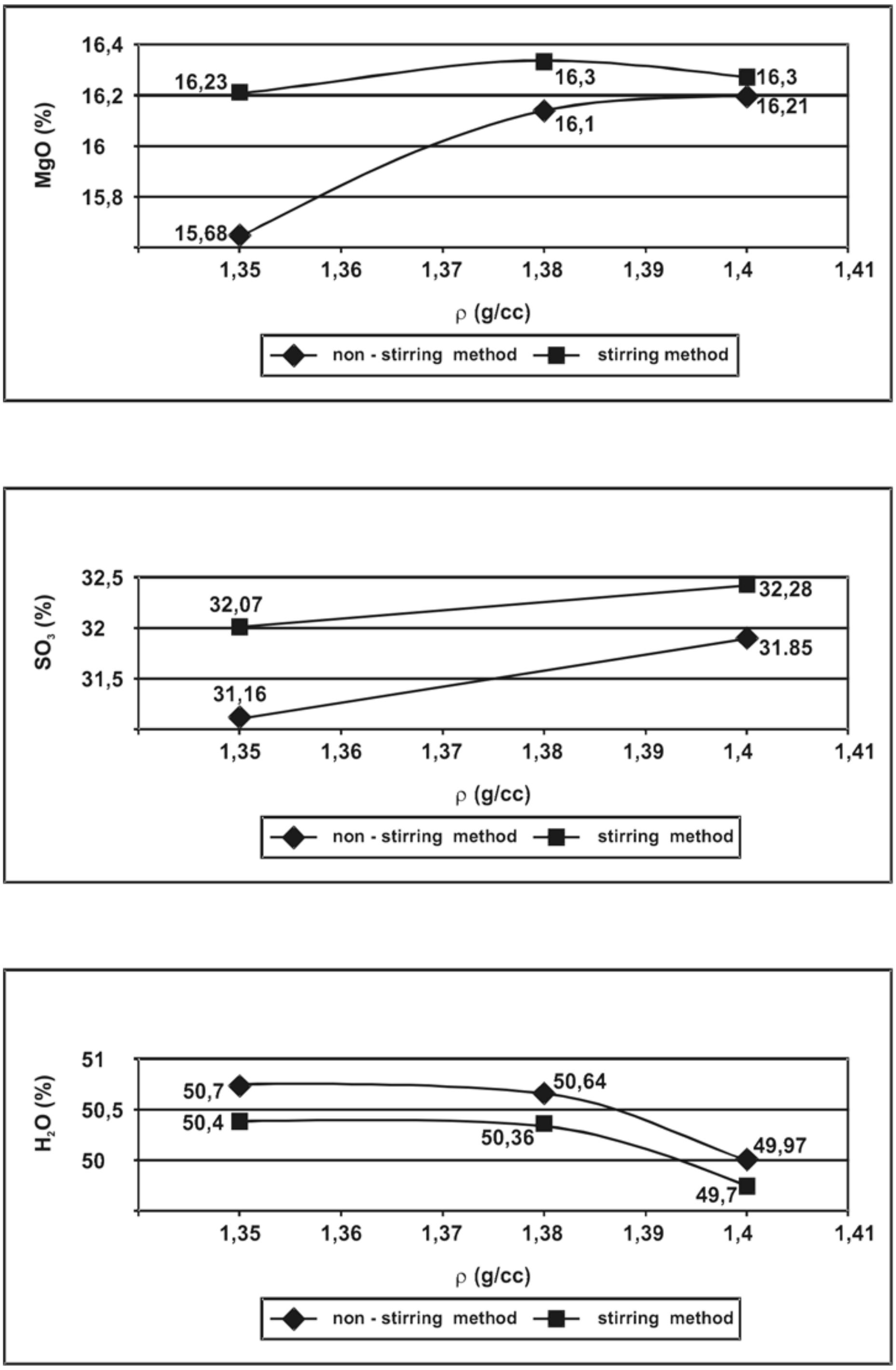

Figure 4. Correlation between MgO, SO_3 and H_2O contents with $MgSO_4.nH_2O$ density, showing the bigger the density the bigger the MgO and SO_3contents and the lesser the H_2O content

Figure 5. Epsomite crystal derived from laboratory tests showing relatively fibrous structure (black arrow)

Process to make epsom salt includes stirring and non-stirring methods. Optimum condition for both methods is slightly different, notably in $MgSO_4.7H_2O$ crystallization temperatures. Crystallization using the former occurs at 15 or 20°C while similar process by the later takes place only at 20°C. Feed density employed for stirring method is the same as that for non-stirring method, namely 1.35 g/cc. Yet products come from both methods have satisfied specification demanded by markets.

The 97 - 98 % of magnesium sulfate heptahydrate content is suitable for several industries such as printing and dyeing thin-cotton fabric, ballast agent for cotton and silk, manufacturing mother-of-pearl and goods from leather, manure, porcelain, pigment, explosives, refractory material as well as material for matches.

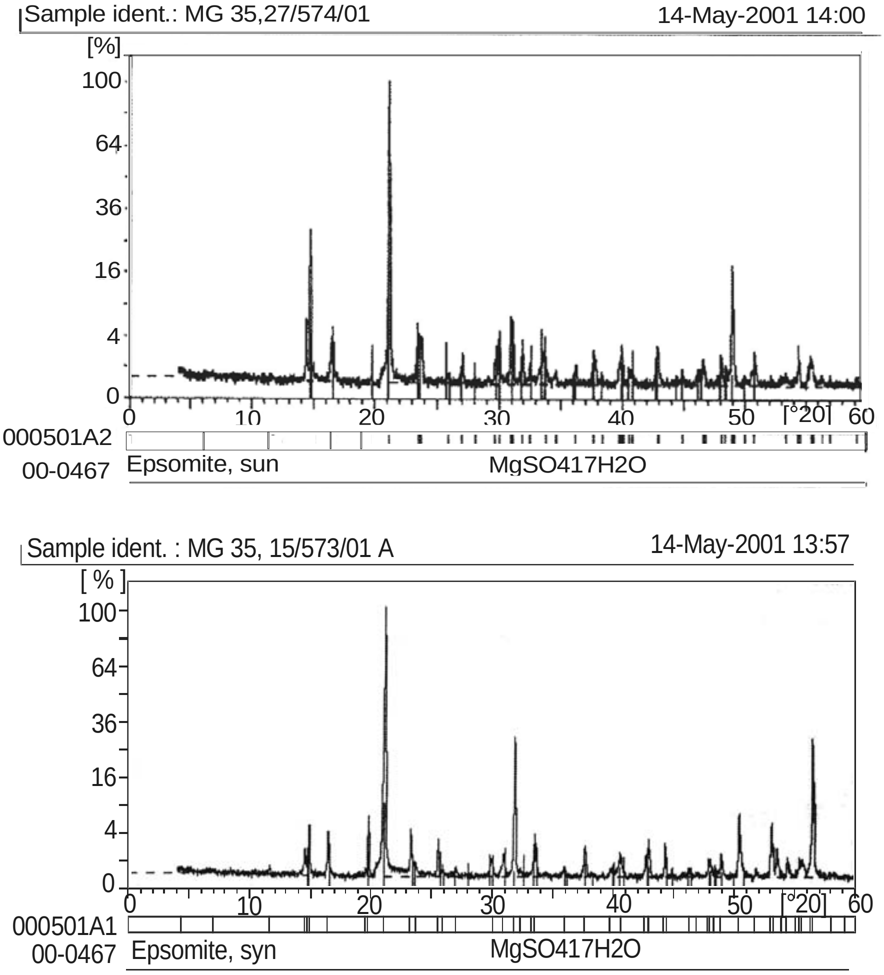

Figure 6. XRD analysis for $MgSO_4.7H_2O$ crystal derived from magnesium sulfate solution with density of 1,35 g/cc and crystallization temperature of 27°C (above) and 15°C (below)

5. CONCLUSIONS AND SUGGESTIONS

Both stirring and non-stirring methods yield relatively significant epsom salt recoveries. However, making epsomite by stirring method is much better than that of non-stirring one. $MgSO_4.7H_2O$ crystallization process using the former is faster than that of the later and results in more evenly crystal formation. In addition, it is known that the bigger the magnesium sulfate density used as the feed the bigger the MgO and SO_3 contents within $MgSO_4.7H_2O$ crystal. However, water content is getting lesser and lesser.

Market requires product specification that includes 97 - 98 % $MgSO_4.7H_2O$. The produced magnesium sulfate heptahydrate crystal contains MgO content that has satisfied such specifications and can be used for manufacturing several materials such as printing and dyeing thin cotton fabric, ballast agent for cotton and silk, manufacturing mother-of-pearl and goods from leather, manure, porcelain, pigment, explosives, refractory material as well as material for matches.

The facts that rate of $MgSO_4.7H_2O$ crystallization is faster and yielded product is evenly distributed make the stirring method for industrial - scale epsomite making is more appropriate than non-stirring method. Such a method will save production cost economically moreover if supported by easy raw material supply. In terms of having desired crystallization temperature – moreover during post evaporation process, the process has to be supported by a good cooling system.

Advanced studies on synthetic dolomite-based epsom salt making need to be conducted. A good quality of laboratory-scale research for epsomite making can then be applied to be used in industrial scale. Dolomite, raw material for producing $MgSO_4.7H_2O$, is relatively abundance in Indonesia and not yet benefited properly. Moreover, there is an in-between product when using dolomite for making epsom salt, namely kieserite – a material which can be employed for fertilizer. Depends on market condition, industries can select whether making epsomite or just producing kieserite or maybe yielding both of them.

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