Magnesium Utilization In Dolomite Rocks By Struvite Precipitation In An Insulated Column Reactor

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Abstract.

Dolomite is a natural mineral rock with the chemical formula $CaMg(CO_3)_2$. Pure dolomite contains 21.70% calcium and 13.04% magnesium. Dolomite has not been widely used in the industrial sector until now. One way to increase the economic value of dolomite rock is to utilize its magnesium content as a precursor to struvite mineral which is the raw material for slow release fertilizer. Under alkaline conditions, struvite minerals are formed at concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-}. Struvite solution (MAP) can be prepared by reacting phosphoric acid, ammonium hydroxide, and dolomite as a magnesium source in a molar ratio of 1:1:1. In a continuously operated isolated column reactor, the pH ranged from 8 to 12, and the reactor inlet air velocity ranged from 0.25 to 1.25 L/min. The chemical elements of dried struvite were determined using XRF (X-Ray Fluorescence), and the morphology was analyzed using SEM (Scanning Electron Microscope). At the same time, the crystal phase composition was identified using the Rietveld XRD (X-Ray Diffraction) technique. Based on the results of XRF analysis, the highest magnesium content was found under operating conditions with pH 12, air rate 0.75 L/min, and magnesium content 15.5%.

Keywords: *Dolomite, isolated column reactor, magnesium and struvite.*

I. INTRODUCTION

The potential of dolomite in Indonesia is huge and significant with diverse specifications [13]. Dolomite combines two minerals: magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$). Dolomite can decompose into oxide compounds in the form of MgO and CaO, widely used in various industrial applications. MgO can be used as an insulator as a high temperature refractory brick material, cement mixture, medical industry, and fertilizer. While CaO is widely used in the cement and chemical industries for the manufacture of certain compounds [14].Dolomite can be found in limestone. Limestone is composed of the minerals calcite and dolomite. Both minerals are relatively soluble in water at a partial pressure of 10 -3 bar, the solubility of calcite is 100 mg/L, and dolomite is 90 mg/L, while at a partial pressure of 10 -1 bar, the solubility of calcite is 500 mg/L, and dolomite is 480 mg/L at pH = 7. Both minerals are composed of calcium and magnesium which have similar physical and optical properties making them difficult to distinguish [4]. Dolomite contains enough Mg to be used as a precursor material for struvite formation. Struvite is an inorganic mineral crystal used as a slow release fertilizer (SRF) [6].

Struvite crystallization occurs under alkaline conditions with equimolecular concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-} based on the following reaction [10] :

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 .6H_2O \quad (1.1)$$

When the Ion Activity Product (IAP) of Mg^{2+}, NH_4^+, and PO_4^{3-} is greater than the solubility product constant (KSP), struvite will be formed [2].

The formation of solid particles in a homogeneous phase is known as crystallization. If a solid dissolves excessively (out of equilibrium), the system will seek equilibrium by crystallizing the dissolved solid [9]. The crystallization process has two main events: nucleation and crystal growth. The formation of crystal nuclei from solution is called nucleation. According to the nucleation theory, once the solubility of the solution has passed (the solution becomes supersaturated), the molecules begin to agglomerate and form clusters. The cluster will eventually grow until it reaches a critical size, referred to as the critical cluster. Adding more molecules to the critical cluster results in the formation of a core crystal (nucleus). The cluster must resist the tendency to dissolve back into a stable crystal core [15]. According to (Anggrainy *et al*., 2014), the time required for the nucleation process to occur decreases with increasing solution pH, temperature, and degree of supersaturation. As with the nucleation process, physical and chemical characteristics such as solution pH, degree of saturation, stirring, crystallization size, temperature, and the presence of interfering ions in the solution greatly affect crystal growth.

Factors that affect the formation of struvite:

1. pH of solution

The effect of pH solution is an important factor in the formation of struvite crystals. The higher the pH of a solution, the more precipitates will form crystals [11]. Increasing pH can also increase the solubility of magnesium and phosphate, which in turn can increase supersaturation and struvite formation.

2. Effect of Molar Ratio

In theory, the molar ratio of Mg:N:P reactants is 1:1:1. One of the parameters that can affect the formation of struvite crystals is the molar ratio of PO_4 reactants and Mg ions. At a certain pH, increasing the molar ratio of Mg:PO_4 reactants will increase the degree of saturation of struvite formation and the percentage of PO_4 removal in solution [3].

3. Aeration Level

Aeration aims to accelerate the process of achieving homogeneity and the formation of struvite crystals [11].

Homogeneity of the solution can be achieved by introducing fine air bubbles and letting them rise through the water (air into water).This study investigated the use of dolomite-derived magnesium as a component in the production of struvite mineral by varying the pH of MAP solution and air rate in continuous struvite synthesis in an isolated column reactor. Magnesium is a macronutrient that plants need in large quantities, so this study aims to obtain struvite material with the highest magnesium composition as a constituent of slow-release fertilizer. In addition, the high magnesium content in struvite also indicates the amount of magnesium removal in dolomite.

II. METHODS

Materials

The materials used in this study are Dolomite (obtained from CV. Globalindo Internusa in powder form with a size of 100 mesh and contains 38% magnesium). $H_3 PO_4$ 98% in a liquid phase, NH_4OH 21% in a liquid phase, and NaOH for alkali source were obtained from Bratachem Chemical Industry. Aquadest was produced using a demineralized water system from the materials laboratory of UPN "Veteran" East Java. All these materials were used without further purification.

Procedure

The equipment used in this study is the same as we have done in our previous studies [8]. This set of equipment consists of several parts, and the center is a vertical column reactor (e) equipped with a bulkhead (f) that functions as a stirrer. This column reactor has a volume of 498.75 mL with a height of 50 cm, an outer diameter of 5 cm, and an inner diameter of 2.5 cm. The bottom of this reactor is connected to a three-neck flask (h) which functions as a container for struvite deposits. In addition, the bottom of the reactor is also connected to two valves, one of which is a place for air flow to enter and is also equipped with a barometer (g). The other valve is connected to the struvite solution reservoir (j). The top of the reactor is also connected to the MAP overflow storage tank (k). The feed enters from the top of the reactor where tank (a) is the MAP feedstock tank, and tank (b) is the NaOH solution tank, each of these feedstock tanks is equipped with pumps (l,n) and overflow tanks for raw materials (m,o). MAP and NaOH solutions enter the reactor through valves (c) and (d). This Isolated Column Reactor works continuously with the principle of countercurrent flow.

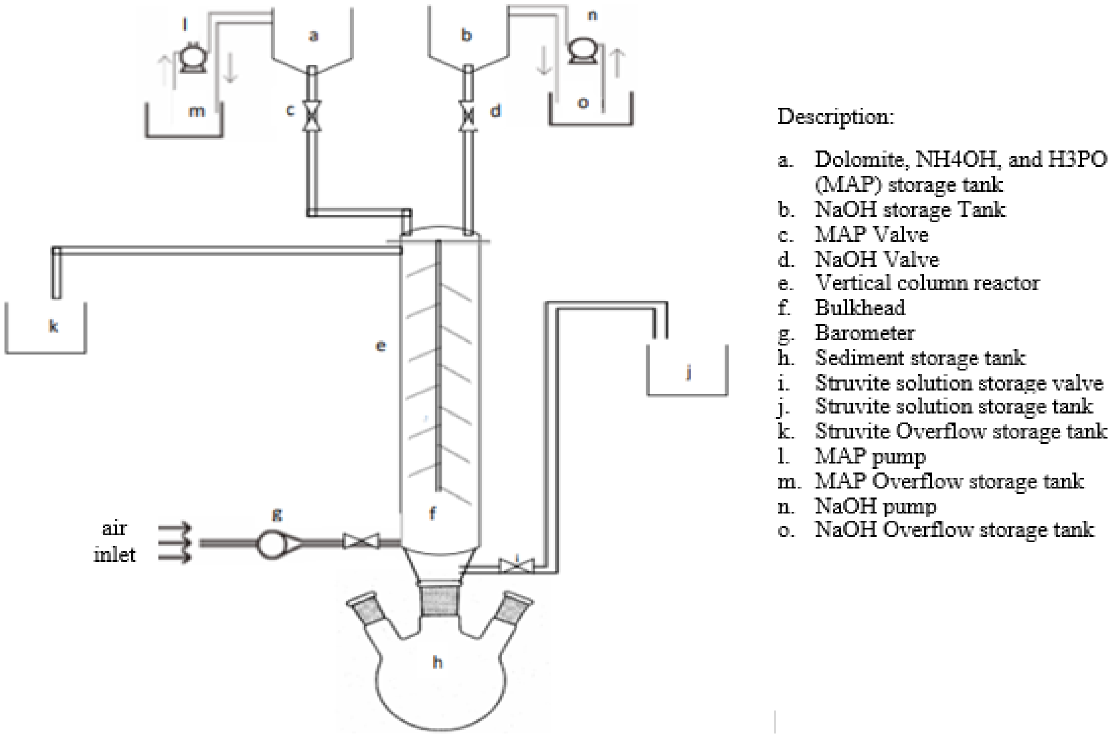

Fig 1. Isolated Column Reactor

The struvite formation process was carried out in the Isolated Column Reactor as shown in Figure 1. continuously. Initially the MAP solution was made by mixing dolomite as a magnesium source, NH_4OH, and H_3PO_4 with a molar ratio of 1:1:1. NaOH solution was also prepared as a pH controller. These two solutions were put into tanks a and b. After the raw materials filled three-quarters of the reactor column, air was introduced from the bottom of the reactor with variations in the inlet air flow velocity (0.25, 0.5, 0.75, 1, and 1.25 L/min). The process was carried out until it reached steady state. After the process, the struvite deposits were filtered and dried and characterized by XRF, SEM, and XRD.

Characterization

Scanning Electron Microscope (SEM) (Evo MA 19 Carl Zeiss, UK) was used to examine the morphology of the struvite material. X-Ray Fluorescence (XRF) (PANalytical, Almelo, Netherlands) was used to determine the chemical constituents of dried struvite. At the same time, X-Ray Diffraction (XRD X'pert PRO PANalytical, Almelo, Netherlands) was used to determine the crystal phase composition in the struvite product.

III. RESULT AND DISCUSSION

The Mg component of the struvite obtained from the experiment was determined using XRF under various conditions. Table 1. displays the XRF results of struvite with varying magnesium content. The highest percentage of magnesium was found at pH 12, with an air flow rate of 0.75 L/min. The lowest percentage of magnesium was obtained at pH 8 with an air flow rate of 0.25 L/min. XRF data is also presented in graphical form, as shown in Figure 2 and Figure 3. To make it easier to see the effect of each variable on the magnesium content of struvite minerals.As the air flow rate increases, the magnesium content extracted also increases. Mg content for pH 8, 9, 10, 11, and 12 generally increased at an air rate of 0.75 L/min and decreased at an air rate of 1.25 L/min. If the air rate is too high, it will cause collisions between particles very quickly so that it can cause the struvite formation process to be unstable. According to (Fitriana and Warmadewanthi, 2016), a faster air rate can cause a decrease in induction time but decrease the stability of struvite, so that magnesium removal will decrease and can cause rupture of struvite crystals, damaging the morphology of the struvite crystal itself. The best air rate according to (Rahman *et al.*, 2014) on struvite formation is 0.73 L/min. From the results of the XRF graph analysis, it was found that the largest magnesium content was found at an air rate of 0.75 L/min.

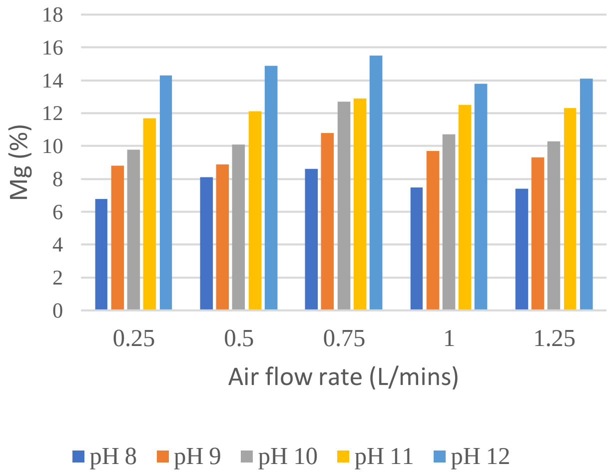

Fig 2. Effect of air flow rate (L/min) on Magnesium content (%) at different pH levels

Figure 3 shows that increasing pH will increase the magnesium content in struvite minerals. The best condition was obtained at pH 12 and air velocity 0.75 L/min. Dolomite material requires a higher pH to produce struvite with the highest magnesium content, where initially the best pH for struvite formation ranges from pH 9.5-10.5 and increases to pH 12 [7]. The increase was caused by the high calcium content. Where Ca affects the formation of struvite crystals, in addition to crystal morphology (Figure 4) it can also affect the pH of struvite crystal formation, where H^+ ions are released during struvite crystal formation.

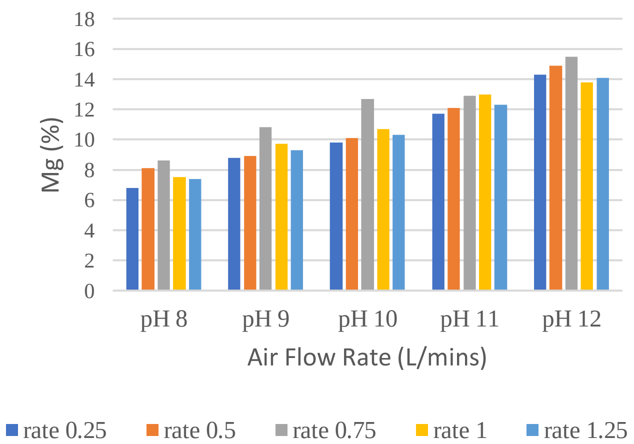

Fig 3. Effect of pH on Magnesium content (%) at different air flow rates (L/min).

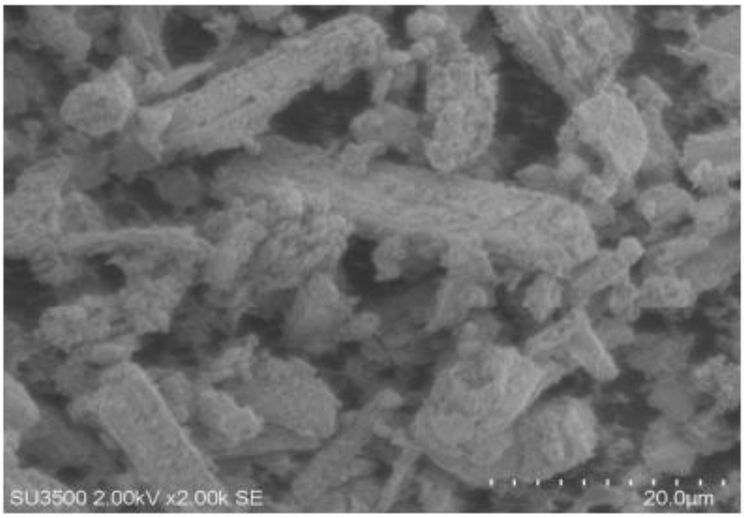

Fig 4. SEM result of struvite crystals at pH 12 with 0.75 L/min air rate.

Table 1. X-Ray Fluorescence (XRF) analysis results of struvite mineral composition

pH	Component %	Air Flow Rate (L/mins)				
		0,25	0,5	0,75	1	1.25
8	mg	6.8	8.1	8.6	7.5	7.4
9	mg	8.8	8.9	10.8	9.7	9.3
10	mg	9.8	10.1	12.7	10.7	10.3
11	mg	11.7	12.1	12.9	12.5	12.3
12	mg	14.3	14.9	15.5	13.8	14.1

According to current theory, struvite crystals have an orthorhombic shape. This study produced an orthorhombic crystal form with small clumps. Where the influence of Ca causes clumping. It is known that Ca in solution affects the growth rate of crystalline compounds, this is due to the blockage of the place where the crystals are formed, thus inhibiting the growth of struvite [7].

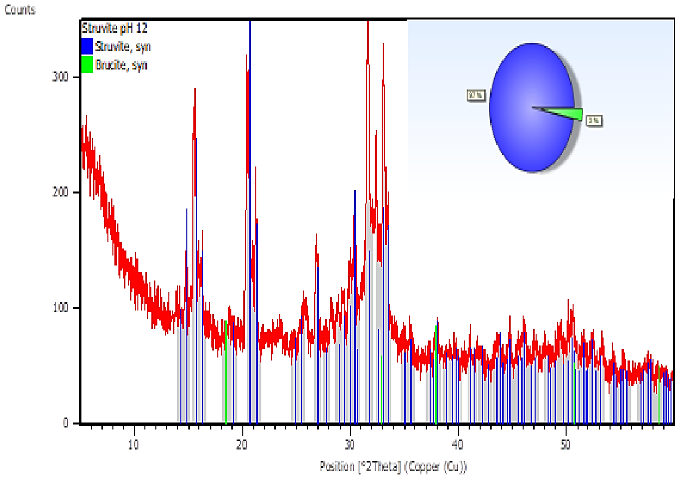

Fig 5. XRD result of struvite materials at pH 12 with air rate of 0,75 L/min.

The existence of a peak graph in the XRD analysis results indicates the formation of struvite material. Based on the findings of the XRD analysis, the struvite material produced from dolomite is not pure. Dolomite contains magnesium elements, and other materials cause the formation of other minerals. The results of XRD analysis of struvite material at pH 12 and air velocity of 0.75 L/min produced 97% struvite and 3% brucite.

IV. CONCLUSION

Based on the results of the study, it can be concluded that the higher the air flow rate can increase the acquisition of extracted magnesium. This can be explained through the principle of mass transfer. As the air flow rate increases, turbulence within the extraction system also increases. This turbulence increases the contact between the washing solution (usually water) and the dolomite rock particles, allowing more magnesium to be dissolved and carried away by the wash solution. Likewise, pH also plays an important role in determining magnesium recovery. The magnesium content extracted at the same airflow rate is higher at higher pH levels. This shows that the solubility of magnesium in water is affected by pH as well.

This can be explained as follows,

- When a lower pH is used, hydrogen ions (H^+) dominate the solution where they can compete with magnesium ions (Mg^{2+}) for bonding sites on the dolomite rock surface, thus inhibiting magnesium extraction.
- If a higher pH is used, the concentration of hydrogen ions decreases and less competition occurs, allowing more magnesium ions to be dissolved into the washing solution.

Thus, air flow rate and pH are the two main factors that can affect magnesium recovery from dolomite rock. However, other factors can be added in improving magnesium recovery including dolomite rock type, operating conditions, and analysis methods, effective optimization strategies can be developed to improve the efficiency of magnesium extraction process. And the best conditions for struvite formation from dolomite rock at pH 12 and air velocity 0.75 L/min, with a magnesium content of 15.5%.

V. ACKNOWLEDGMENTS

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