

Pemurnian Batu Kapur Berbasis Nano Kalsit dengan Metode Kopresipitasi

Purification of Nano Calcite Based Limestone with Coprecipitation Method

Nugrahani Primary Putri*, Diah Hari Kusumawati
Jurusan Fisika, Fakultas Matematika dan Ilmu Pengetahuan Alam
Universitas Negeri Surabaya

ABSTRAK

Sintesis nano kalsit yang terbuat dari batu kapur menggunakan metode kopresipitasi berhasil diimplementasikan. Sintesis dilakukan dengan memvariasikan tekanan gas CO₂ dan waktu pengendapan untuk mendapatkan kalsit dengan kemurnian tinggi dan ukuran partikel kecil. Data difraksi dikumpulkan menggunakan XRD, yang kemudian dianalisis menggunakan perangkat lunak Match dan Rietica untuk mendapatkan informasi tentang kecocokan, tingkat kemurnian, kepadatan, dan ukuran partikel. Dari analisis menggunakan Match, ditemukan sampel yang disintesis dengan metode kopresipitasi memiliki fase kalsit. Hasil analisis berdasarkan Rietica menunjukkan bahwa hasil terbaik adalah sampel yang disintesis dengan variasi tekanan gas CO₂ 37,5 kgf/cm³ dan waktu pengendapan selama 36 jam.

Kata Kunci : nano kalsit, batu kapur, kopresipitasi

ABSTRACT

Synthesis nano calcite made of limestone using coprecipitation method has been successfully implemented. Synthesis is held by varying the CO₂ gas pressure and precipitation time in order to obtain calcite with high purity and small particle size. Diffraction data were collected using a XRD, which then analyzed using software Match and Rietica to obtain information about fitness, degree of purity, density and particle size. From analysis using Match, it was found that limestone as base material has CaCO₃ and Ca(OH)₂ phases, while samples which synthesized by coprecipitation method has calcite phase. Analysis result by Rietica shows that the best result is sample which synthesized with CO₂ gas pressure variation of 37.5 kgf/cm³ and the settling time for 36 hours.

Key words: nano kalsit, lime stone, kopresipitasi

INTRODUCTION

Calcium carbonate (CaCO₃), or better known as limestone, has been widely used in various fields, such as construction, health, industry, and food. In the construction, calcium carbonate is used as a building material. For broader applications, calcium carbonate is formed into nanoparticles that have superior properties. Nanoparticles calcium carbonate can be used as filler in anti-corrosion material and has good anti-corrosion properties when compared with its original material (Olad and Rashidzadeh, 2008).

In addition, CaCO₃ nanoparticles can also be used as a mixture of cosmetics, drug delivery, to food nutrition. Processing of raw materials to obtain Calcium carbonate can be in two ways, namely, ground calcium carbonate (GCC) and precipitation (Apriliani *et al.*, 2012). The results obtained from the precipitation process have superior properties and can be used in the food and pharmaceutical industries. Indonesia as a country that has abundant natural wealth, has a source of basic

Ingredients of calcium carbonate, among others, limestone, shells and egg shells. Limestone is a basic material that is easy to obtain, easy processing and the price is relatively affordable. In general, minerals contained in limestone are calcite 95%, dolomite as much as 3%, and the remainder is mineral clay (Apriliani *et al.*, 2012). So far, limestone is only used as one of the building materials without any further process. Several studies have successfully obtained calcium carbonate using both precursors (Olad and Rashidzadeh, 2008), as well as from natural materials (Apriliani *et al.*, 2012; Herianto, 2005). In this study used as a base material is a lot of limestone obtained around us. The purpose of this research is to optimize purification of calcium carbonate from limestone as well as calcium carbonate synthesis in the form of nanoparticles.

METHODS

Material and Instrumentation

Materials used in this experiment were limestone, distilled water as solvents and carbon

*E-mail korespondensi:
nugrahaniputri@unesa.ac.id

dioxide (CO₂) gas cylinder. The X-ray diffraction (XRD) data were obtained by JEOL 3530 Shimadzu using Cu K α radiation.

Procedures

A 10 g of limestone is fed into 60 ml of distilled water and stirred and rinsed until the debris contained in limestone is lost. The solution is precipitated and the precipitate is then dried at 100 °C for 1 hour. After drying, the precipitate is mixed into the distilled water with a weight ratio of 1: 6, then flowed with carbon dioxide gas with a pressure variation of 22.5; 30 and 37.5 kgf/cm³. After the gas is fed, the solution is then precipitated by a settling time varied for 12, 24 and 36 hours. The precipitate obtained was then filtered and dried in a furnace with a temperature of 100 °C for 1 hour. After drying, the powder obtained was tested with XRD to obtain the phase characteristic data contained in the sample. XRD data was then analyzed using Match and Rietica software to obtain crystal material structure information.

RESULT AND DISCUSSION

This research has successfully synthesized calcium carbonate (CaCO₃) from limestone using

coprecipitation method. Limestone is precipitated (washed) up to 5 times deposition to minimize existing impurities. When limestone mixes with distilled water, chemical reactions are marked by the appearance of air bubbles and increasing the temperature of the solution. This happens because the reaction between limestone and distilled water is an endothermic reaction. After going through the process of precipitation and drying, calcium carbonate is produced in powder form. The obtained CaCO₃ powder has various color gradations, this is due to the influence of CO₂ gas pressure variation and the settling time during the synthesis process. From the color difference, some samples were taken with a whiter than other samples, a sample with a CO₂ gas pressure of 30 kgf/cm³ with variations of precipitation time of 12.24 and 36 hours, herein after called samples 2, 5 and 8 And samples 1 (22.5 kgf/cm³, 12 hours) and sample 9 (37.5 kgf/cm³; 36 hours) as a comparison sample, then be tested with XRD to obtain the phase information contained in the sample. The results of characterization using XRD can be seen in Figure 1.

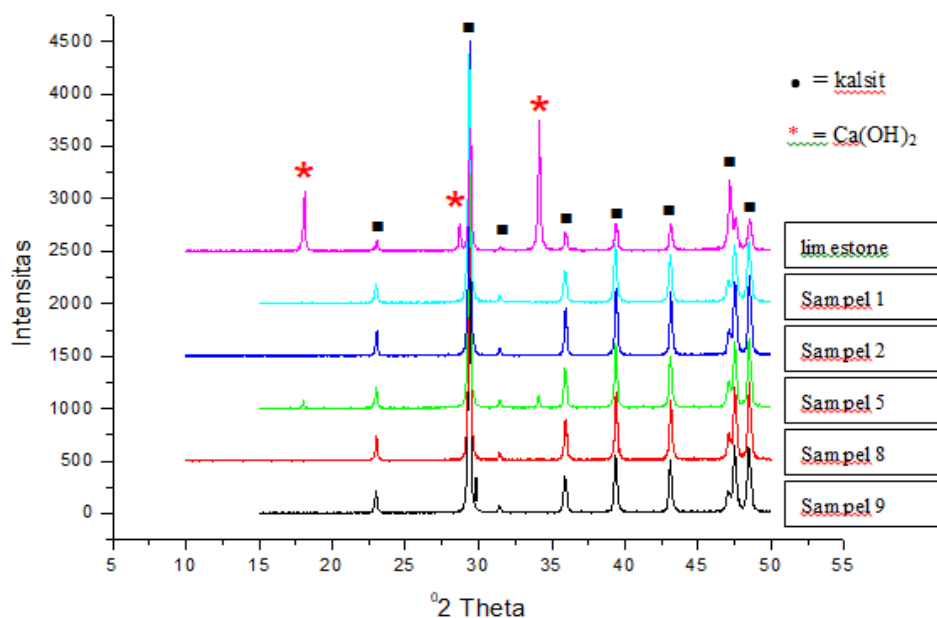


Figure 1. XRD patterns of calcite and calcium carbonate

Figure 1 shows that the variation of CO₂ pressure and settling time causes a peak change between the limestone sample and the synthesized sample. The limestone as the starting material has calcite peak and Ca(OH)₂ (purple color pattern). The peak of calcite is seen in the 2 θ : 23, 29, 32, 36, and 46 positions, whereas the Ca(OH)₂ peak is seen

at 2 θ : 15, 28 and 34. After obtaining the CO₂ gas stream, in samples 1, 2, 8, And 9 is no longer found Ca(OH)₂ peak, remaining is the peak of calcite at position 2 θ in accordance with ICSD code 16710. The loss of Ca(OH)₂ peak is due to the bond between Ca(OH)₂ and CO₂ to CaCO₃. In sample 5, in addition to calcite peak, Ca(OH)₂ peak was still at

2 θ : 15 and 34 but with lower intensity. This is because there has not been a perfect reaction so that there is still Ca(OH)₂ that has not bind to CO₂ gas.

Rietica analysis was performed to obtain the purity, density and sample crystal sizes tested XRD as seen from the output obtained. The analysis begins with making a calculated model and then refine it with a measurable model (sample). There are 2 types of output obtained, the first is a matching graph between the model and the sample.

If the calculated and measured model analysis results show a match, then the sample is a calculated model phase. The output data from the analysis by the Rietveld method will show the matching level of the XRD result with the model that has been made. The match rate indicator can be seen from the figures-of-merit (FoMs), which is said to be suitable if it has a goodness-of-fit (GoF) of less than 4% (Pratapa, 2007). The output of rietveld analysis for all samples can be seen in table 1.

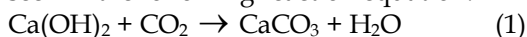
Table 1. Output parameter of Rietveld refinement for all sample

Sample	Figures-of-merit (FoMs)				Phase Scale Factor	
	Rp	Rwp	Rexp	GoF	CaCO ₃	Ca(OH) ₂
Limestone	14,46	20,75	15,13	1,88	0,00007485	0,003361
Sample 1	19,1	24,58	13,37	3,38	0,00015081	-
Sample 2	17,27	22,58	14,11	2,56	0,00016653	-
Sample 5	15,17	20,31	13,33	2,32	0,00015671	0,000489
Sample 8	17,82	23,96	14,16	2,86	0,00017221	-
Sample 9	20,31	29,75	16,09	3,42	0,00015375	-

It can be seen that GoF values for all samples cost less than 4% so it can be concluded that Rietveld's analysis has been done correctly. The second is output data containing information on density, crystal size and weight ratio when the phase is analyzed more than one. The results of Rietica's analysis of limestone and synthesized samples can be briefly seen in Table 2 below.

From Table 2 it can be seen the effect of CO₂ pressure and settling time on purity, density and calcite crystal size of limestone synthesis result by coprecipitation method. As a starting material, limestone has calcite and calcium hydroxide content (Ca(OH)₂) with a purity ratio of 54.84%

calcite: 45.16% Ca(OH)₂, density value 2.701 g/cm³ and a crystal size 99,4 nm. With CO₂ gas flowing bonds occur between calcium hydroxide with CO₂ gas to form calcium carbonate, as can be seen in the following reaction equation:



It is proven that after the CO₂ gas flows, the purity of the sample increases. In all major variations of gas pressure, the purity of calcite has reached 100% except in the 30 kgf/cm³ gas pressure variation deposited for 24 hours. At the time of deposition for 24 hours, it can be seen that

Table 2. The Effect of CO₂ Pressure and Time of Precipitation on Purity, Density as well as Sample Crystal Size

Sample	Weight percentage (%)		Density (g/cm ³)		Particle size(nm)	
	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂
Limestone	54,84	45,16	2,701	2,242	99,4	67,7
Sample 1	100	-	2,702	-	93,3	-
Sample 2	100	-	2,694	-	103,6	-
Sample 5	94,57	5,43	2,706	2,244	104,2	95,2
Sample 8	100	-	2,699	-	103,6	-
Sample 9	100	-	2,703	-	85,5	-

calcite purity decreased slightly when compared with other sedimentation times, although still above 90%. Sample 5, ie a sample with a 30 kgf/cm³ CO₂ gas pressure deposited for 24 hours, has the smallest purity, density and largest crystal size when compared with other samples. This may be due to the presence of the remaining calcium hydroxide phase of the Ca(OH)₂ reaction

with CO₂ gas. The presence of calcium hydroxide can affect the measured density and size of the XRD characterization. With the variation of sedimentation time, it can be seen that the density of calcite is in the range of 2,694 - 2,706 g/cm³ which has close to the theoretical density calcite value that is equal to 2,71 g/cm³.

Figure. 2 is a graph of the relationship between precipitation time to the magnitude of the purity and the size of the calcite crystal of the reaction product. It can be seen that at 30 kgf/cm³ CO₂ gas pressure, the smallest crystal size (103.6 nm) is at 12 and 36 hours precipitation time. The size of the crystal is not the expected maximum result because it is still below 100 nm. Table 5.1 The best performing sample was a 100% purity sample and the smallest crystal size (85.5 nm)

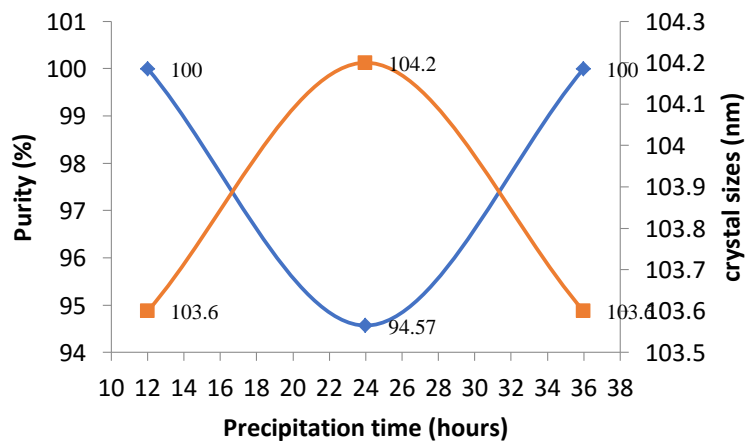


Figure 2. Effect of precipitation time on purity and crystal sizes at 30 kgf/cm³ CO₂ gas pressure

ACKNOWLEDGEMENTS

Acknowledgments are given to the manager of Energy Laboratory ITS Surabaya for assistance in XRD characterization.

REFERENCES

- Apriliani NF, Baqiya MA, Darminto, 2012. *Jurnal Sains dan Seni ITS*, 1(1).
- Olad A and Rashidzadeh A, 2008. *Iranian Journal of Chemical Engineering*, 5(2).
- Herianto, Edi, 2005. *Prosiding Seminar Material Metalurgi*. Serpong.
- Pratapa S, 2007. *Makara Sains*. 11(2), November

obtained in a pressure sample of 37.5 kgf/cm³ and a precipitation time of 36 hours (sample 9).

CONCLUSION

From the results obtained can be concluded that the optimum results obtained in the sample after the pressure of CO₂ gas amounted to 37.5 kgf/cm³ and the settling time for 36 hours.