Precipitation Rate Investigation on synthesis of precipitated calcium carbonate

E Sulistiyono¹, M Handayani¹, F Firdiyono¹ and E N Fajariani²

¹Research Center of Metallurgy and Materials, Indonesian Institute of Sciences (LIPI), Tangerang Selatan, Banten, 15314, Indonesia
²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, 57126, Indonesia

E-mail: eko221068@gmail.com

Abstract. Study on the formation of precipitated calcium carbonate from natural limestone Sukabumi with the influence of various parameters such as precipitation rate, concentration of CaCl₂ and amplitudes were investigated. We also investigated the result with the precipitated calcium carbonate from Merck (p.a) for comparison. The higher concentration of CaCl₂ would give effect to the lower of the precipitation rate. It was observed that precipitation rate of calcium carbonate from limestone Sukabumi at concentration of 0.08 molar was 3.66 cm/minutes and showing the optimum condition, while the precipitation rate of calcium carbonate Merck at the concentration 0.08 molar was 3.53 cm/minutes. The characterization of precipitated calcium carbonate was done using X-ray fluorescence (XRF) and scanning electron microscope (SEM). The characterization using XRF showed that CaO content of precipitated calcium carbonate from natural limestone Sukabumi had high purity of 99.16%. The particle distribution using scanning electron microscope (SEM) showed that precipitated calcium carbonate from natural limestone Sukabumi revealed 1.79 μm – 11.46 μm, meanwhile the particle distribution of precipitated calcium carbonate Merck showed larger particles with the size of 3.22 μm – 10.68 μm.

1. Introduction

Sukabumi district has abundant mineral resources, one of the mineral resources is limestone. Potency of limestone in Sukabumi is in Cibadak area, Gunung Guruh Jampang Tengah, Cisolok, Cikidang and Warung Kiara [1]. Until now, the utilization of limestone in Sukabumi regency is used as building materials such as bricks and cement materials [1].

Calcium carbonate is a chemical compound with chemical formula of CaCO₃, which is a major component of the shell of marine organisms, snails, pearls and eggshells [2]. The primary forms of limestone is from sedimentation process of snails shell of small fossils, shells, and coral for millions of years [3]. The physical properties of calcium carbonate such as morphology, phase of size and size distributions must be modified according to the applications. Morphological form and phase of calcium carbonate associated with synthesis conditions such as concentration of reactant, temperature, time and natural addictive substances [3].
Besides as building materials, calcium carbonate is widely used as main raw materials in various industries of paints, inks, paper, plastic, cosmetics, nutritional supplements, polymer pipes and fillers for composit materials [3]. In technological developments, nano-size calcium carbonate materials can be utilized as filler of natural rubber which can provide superior properties of rubber materials[4].

Precipitated calcium carbonate is made through two paths. First path is the process path of dissolution using chloride acid and sodium carbonate precipitation [5]. Second path is calcination process of limestone and then dissolved the calcination result in water and added by carbon dioxide gas [6]. Preparation of calcium carbonate by dissolution and precipitation can be modified by the addition of dodecyl dimethyl betaine material which can produce nano-size calcium carbonate [7]. This article presents experiment result of making precipitated calcium carbonate of limestone from Cibadak, Sukabumi. The process used was dissolution process of limestone in solution of hydrochlorida to form calcium chloride and a little impurities. After that, solution of calcium chloride was purified from impurities and then re-precipitation was done using solution of sodium carbonate to form precipitated calcium carbonate.

2. Experimental

2.1. Raw materials
The raw materials for this experiment were limestone from Cibadak, Sukabumi. Samples were taken from hill locations of traditional mining area of limestone which adjacent to limestone combustion units. The limestone that has been selected was subsequently crushed into a fractional shape with a size of approximately 1 cm so that the dissolution process using hydrochloride acid does not take place so quickly. The limestone subsequently partially crushed until smooth for doing analysis of raw materials. In this experiment, the limestone used was raw limestone without heating or calcination. The raw materials of limestone which has the best quality based on X-Ray Fluorescence (XRF) analysis with CaO content around 93% and has white colour was used for further experiments.

2.2. Experimental procedure
The natural limestone for experiment was obtained from Cibadak, Sukabumi district. 200 g of limestone was added in dilute HCl solution. Dilute HCl solution was prepared by mixing 350 ml of concentrated HCl 37% (Merck) with aquadest to a volume of 2 liters. Reaction process will form turbid solution with brown color. Turbid solution was filtered forming a clear yellow solution and then the solution was neutralized with ammonium hydroxide to get solution with pH of 7. Solution then was filtered again using Whatman filter paper No. 42 obtaining clear yellow solution. The solution was subsequently diluted to obtain 1 molar of calcium carbonate solution.
Calcium carbonate solution was then diluted into 0.04 mol, 0.08 mol, 0.12 mol, 0.16 mol and 0.2 mol. After that, weight of Na₂CO₃ needed for precipitation was determined and obtained 4.7062 g; 9.4116 g; 14.1185 g; 18.82496 g dan 23.5312 g. After that, the precipitation process was conducted so that white solid calcium carbonate with very fine grain size was resulted. Precipitation process was done by mixing and stirring 100 ml of calcium carbonate solution with 10 ml of sodium carbonate solution at room temperature. The precipitate obtained was then filtered and washed with aquadest, it did not need to be dried. Precipitation rate investigation was performed by taking precipitate of calcium carbonate added in 200 ml of aquadest. After that it was shaken until evenly and then poured in a large-sized reaction flask. Investigation for decreasing of height level of sedimentation was done by palcing the flask in the upright stand. The process was repeated with different variable of concentration of calcium carbonate. Besides that, we measured precipitation rate of calcium carbonate from commercially available calcium carbonate (Merck) for comparison. After optimum point of measurement was obtained, the sample was then analyzed using scanning electron microscopy (SEM) to know grain size of precipitated calcium carbonate.
3. Result and Discussion

3.1. Analysis of dissolution process with HCl and precipitation process of calcium carbonate

A series of experiments of dissolution process of calcium carbonate from Cibadak, Sukabumi with HCl was performed and compared with calcium carbonate from commercially available (Merck). Experiment result showed that calcium carbonate from natural materials of limestone contained a lot of impurities. From the observation, it can be seen that the limestone produced the turbid solution due to the presence of impurities that did not dissolve in dilute HCl solution. After filtering and cleaning process of the impurities, it was seen that the solution was yellow colour which indicated the impurity contained metal ion. This result was different with calcium carbonate from merck which gave a brighter colour. The colour difference of calcium carbonate from natural limestone and commercially available (Merck) could be seen in Figure 1.

![Figure 1. Dissolution process of calcium carbonate with HCl. Dissolution process of natural limestone (left), Colour solution of sodium chloride which showed yellow colour for natural limestone and clear for Merck (right)](image)

The result of analysis using XRF for natural limestone was shown in Table 1. It was depicted that dissolution process of calcium carbonate could increase the content of CaO from 93.44 % (before process) into high purity of CaO content of 99.16 % (after process). This result indicated that impurities were considerably reduced impurities, even several impurities were undetected such as magnesium, silica, alumina and iron. For the comparison, we measured calcium carbonate from Merck using XRF and the analysis result showed that CaO content was 99.40 %. This observation revealed that the difference of CaO content of natural limestone was not large compared with CaO from Merck so that the process was efficiently reduced the impurities and obtained high purity of precipitated calcium carbonate.

| Component | Before Process (%) | After Process (%) | Merck (%) |
|-----------|--------------------|-------------------|-----------|
| CaO       | 93.44              | 99.16             | 99.40     |
| MgO       | 2.06               | Nd                | Nd        |
| SiO2      | 0.85               | Nd                | Nd        |
| Al2O3     | 0.62               | Nd                | Nd        |
| P2O5      | 0.61               | 0.14              | Nd        |
| SO3       | 0.54               | 0.14              | 0.16      |
| K2O       | 0.44               | Nd                | Nd        |
| Cl        | 0.42               | 0.30              | 0.34      |
| Fe2O3     | 0.19               | Nd                | Nd        |
| SrO       | 0.13               | 0.14              | 0.03      |
| BaO       | 0.08               | Nd                | Nd        |

*a laboratory: Faculty of MIPA-UNS. Nd = Not Detected
3.2. Analysis of precipitation rate
Precipitated calcium carbonates were obtained from precipitation process of calcium chloride solution with sodium carbonate. In this research, variations of calcium carbonate concentration were performed. The result of precipitation process was used for measuring precipitation rate on the particle density of calcium carbonate. The result of the experiment showed that the more concentrated calcium carbonate would result precipitation rate slower. Decreasing of precipitation rate was seen in increasing the concentration from 0.04 molar to 0.12 molar. However, precipitation rate would diminish after 0.12 molar. It is possible that decreasing of grain size of calcium carbonate was not linear with the increase of concentration, and only gave effect for the arrangement of precipitate in the solution.

![Figure 2. Correlation between precipitation rate of CaCO₃ with concentration of CaCl₂ solution.](image)

Figure 2 showed the similarity of tendency of decreasing the precipitation rate to the increase of concentration on natural limestone from Cibadak, Sukabumi with calcium carbonate from Merck. However, decreasing of precipitation rate started to slow down at 0.12 for calcium carbonate from Merck, whereas decreasing of precipitation rate of precipitated calcium carbonate from natural limestone Cibadak at concentration of 0.16 molar.

3.3. Analysis of distribution size using scanning electron microscopy
Size distribution of participated calcium carbonate from natural limestone was done using scanning electron microscopy (SEM) showed that grain size of calcium carbonate was still quite large when referring to the standard of nanoscale material, where the grain size was still above 100 nm. The particle distribution using scanning electron microscope (SEM) showed that precipitated calcium carbonate from natural limestone Sukabumi revealed 1.79 µm – 11.46 µm, meanwhile the particle distribution of precipitated calcium carbonate Merck showed larger particles with the size of 3.22 µm – 10.68 µm. The result of SEM measurement was depicted in Figure 3.

![Figure 3. SEM measurement result of precipitated calcium carbonate for Merck (left) and for natural limestone from Cibadak, Sukabumi (right).](image)
From the result of SEM analysis with various enlargement (see figure 4), it can be seen that precipitated calcium carbonates have homogenous crystalline form. From the observations at magnification 500 times and 2,000 times, it indicates that the grain arrangement is in the form of cubic shape which shows that the compound is calcium carbonate[2]. By having a homogeneous arrangement of particle shape, the material is already qualified as a good filler material because the structure is uniform.

![Figure 4](image.png)

**Figure 4.** The form of calcium carbonate crystals from the dissolution process of HCl and the precipitation process of natural limestone using Na$_2$CO$_3$ at magnification 500 times (left) and magnification 2,000 times (right).

4. Conclusion

From the results of the above experiments, it can be concluded that limestone from the Cibadak, Sukabumi Regency has the potential to be developed into advanced materials based on calcium carbonate. Through the process of dissolving with chloride acid and precipitating with sodium carbonate solution into product of precipitated calcium carbonate having a very high purity and uniform grain shape and the same molecular structure. From the result of the analysis of the precipitation rate, it can be seen that the point of optimization of the precipitation rate for natural limestone is 0.16 M and the optimum point of calcium carbonate from Merck is 0.12 M. By comparing natural limestone with calcium carbonate from commercially available, the same process produced precipitated calcium carbonates which have almost the same properties. By having a homogeneous arrangement of particle shape, the precipitated calcium carbonate materials are already qualified as a good filler material.

References:

[1] Anonymous 2015 *Year-End Report of Mining and Environment Office of Sukabumi Regency*

[2] Necmettin E, Haci A E 2016 *Physicochem. Probl. Miner. Process.* **53 (1)** 57

[3] Oates J A H 1998 *Lime And Limestone Chem. Tech.* 130-153

[4] Adi C and Norma A K 2012 *Warta Perkaretan* **33 (2)** 113

[5] Kirboga S, Oner M. 2013 *Chem. Eng. Trans.* **32** 1974

[6] Lailiyah Q, Bakiya M, Darminto 2012 *Journal of Science and Arts ITS* **1** 69

[7] Wang C, Liu Y, Bala H, Pan Y, Zhao J, Zhao X, Wang Z 2007 *Colloids and Surfaces A: Physicochem. Eng. Aspects* **297** 179