Hydraulic Activity and Synthetic Characteristics of Precipitated Calcium Carbonate according to Geological Properties of Limestone

Ye-Jin YANG1, Jung-Ah KIM2, Seong-Young NAM3, Jin KIM1 and Ji-Whan AHN2*

1Department of Energy Resources Engineering, Inha University, Incheon 402-751, Republic of Korea
2Technical Research Institute, Posco, Pohang 790-785, Republic of Korea
3Korea Institute of Geoscience And Mineral Resources, Daejeon 305-350, Republic of Korea

Abstract
The objective of this study is to examine the effects of the geological properties of limestone on the synthetic characteristics of precipitated calcium carbonate (PCC) and hydraulic activity. Four groups of limestone samples from eight different limestone deposits according to formation age have been studied. With greater formation age of limestone such as samples from the Paleozoic Ordovician (500~430 million years ago), more calcite twins were presented. Whereas the newest limestone from the Cenozoic Tertiary (65~2 million years ago) had no calcite twins. Furthermore, hydraulic activity and the production yield of aragonite-shaped PCC increased with lower formation age of limestone.

Key words: Limestone, Formation Age, Hydraulic Activity, Aragonite Calcite twins

1. Introduction
Limestone is sedimentary rock, mainly composed of CaCO3 and contains impurities such as Al2O3, SiO2, Fe2O3, MgO and so on. The origin of limestone can be broadly divided into two theories: inorganic origin and organic sedimentary origin. According to inorganic origin, calcium hydrogen carbonates in the state of being dissolved in sea form a calcium carbonates as the temperature raises. Regarding to the organic sedimentary origin, limestone deposits can be formed as debris of organisms deposited and accumulated1,2. Limestone deposits are widely distributed and the amount of limestone reserves is abundant, accounting for about 14% of the earth’s crust and 20~30% of sedimentary rock. Limestone reserves in South Korea are about 6.8 billion tons and mainly concentrated in North Chungcheong Province and Gangwon Province. However, in spite of rich reserves of limestone deposits, high grade limestone that contains more than 52 wt.% of CaO accounts for only about 12% of the total reserves3. Therefore, it is necessary to develop technology for efficient use of limestone and to realize high value-added limestone.

Precipitated calcium carbonate (PCC) is obtained through calcination, hydration, and carbonation and used as a raw material in the paper, paint, rubber, and plastic industries. In particular, the application field and price of PCC are determined in accordance with its crystal size, shape, and purity and its price is hundreds of dollars per ton. However, while research on the field of use and production of PCC has been actively carried out, there has been insufficient study on the influence of characteristics of limestone deposits on synthetic PCC.

Generally, factors such as chemical composition and particle sizes are used to classify limestone, but there is a limit with this alone. For example, particle size and the production yield of aragonite PCC are not constant when using limestone samples that have similar chemical compositions. Hogewoning (2006) studied the influence of the petrographical characteristics of limestone on the hydration activity and reported that the existence of calcite twins in limestone reduced the hydration activity4. Upon this back-
Hydraulic Activity and Synthetic Characteristics of Precipitated Calcium Carbonate according to Geological Properties of Limestone

In the present study, the characteristics of hydraulic activity and the production yield of aragonite PCC according to the formation age and geological properties of limestone by using limestone samples that have similar chemical compositions. It is assumed that the formation age of limestone can vary by up to about 500 million years despite having similar chemical compositions.

2. Experiment Procedure

Eight limestone samples from Korea, Japan, and Belize were collected for this study. Two limestone samples of the Gabsan formation, Jechon area, Cheungbuk were from the early Paleozoic era (500 million years ago) and two limestone samples of the Hongjeom Series, Yeongwol and Jeongsun, Gangwon were from the late Paleozoic era (300 million years ago). In addition, two limestone samples of Belize deposited in three phases of the Cenozoic era (60 million years ago) and two samples of Japan deposited at the beginning of the Mesozoic era (220 million years ago) were used. Limestone samples having similar chemical compositions were used and the chemical components of each limestone ore were analyzed using X-ray fluorescence (XRF; XRF 1700, Shimazu).

The procedure employed for the experiments was shown in Fig. 1. Eight limestone samples with different formation ages were first crushed using a jaw crusher and separated in a range of 19–31.5 mm with a sieve. The separate samples were calcined in an electric furnace at 1000°C for 2 hours to obtain quicklime (CaO). After cooling, quicklime was stored in a vacuum pack and put in a desiccator to suppress reaction with water in the atmosphere.

Quicklime with size less than a 200 mesh was used to conduct the hydration experiments. When quicklime reacts with water, high heat is generated and the formula is expressed as follows in an exothermic reaction.

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 15.59 \text{ kcal/mol} \quad (1)
\]

CaO reacts with water to synthesize Ca(OH)\(_2\) through a hydraulic process, as shown in Fig. 2. The overall experiments were conducted as described in KS E 3077 (Korean Standard Test). Dried CaO(30 g) was put into a reactor for hydration. The temperature of the reactor was fixed at 25°C. Once the temperature of the reactor containing CaO reached a steady state in temperature, distilled water (120 ml) at 25°C was added to the reactor with stirring at 400 rpm for 30 min and the temperature was measured by a thermometer.

Hydraulic activity was measured by KS E 3077 to understand its effect on the distribution ratio of the polymorphs (either aragonite or calcite) in synthetic PCC. KS E 3077 describes the standard method for testing the hydraulic activity of limestone used to PCC synthesis, and a value of hydraulic activity can be calculated by the following equation.

\[
A = T_{30s} - T_0 = \Delta T
\]

where \(A\) : Hydraulic activity (°C) of limestone
\(T_{30s}\) : Temperature (°C) at 30 seconds from the start of hydration
\[ T_0 \]: Temperature (°C) before the start of hydration
\[ \Delta T \]: Value (°C) of temperature change from the start of hydration to 30 seconds

For aragonite synthesis, dry \( \text{Ca(OH)}_2 \) produced by hydration at each condition was used and a synthesis method using \( \text{Ca(OH)}_2 - \text{NaOH-Na}_2 \text{CO}_3 \) solution was introduced. This method was suggested by Kim et al. (2006) as an optimal method to synthesize single phase aragonite. To adjust the \( \text{CO}_3^{2-} \) concentration, 150 ml of 0.5 M NaOH was employed. The reaction temperature and stirring speed were 25°C and 400 rpm, respectively.

After the reaction, each solution was filtered and the filtered precipitate was washed with ethanol three or four times to remove water from its surface. Each precipitate was dried at over 80°C in an oven and then stored in a vacuum pack. Dried materials such as quicklime, calcium hydroxide, and PCC were characterized by X-ray diffraction (XRD; D/Max-1200, RIGAKU). The production yield of synthetic PCC (wt.%) were calculated by Rietveld method (Rietveld method software: HighScore Plus, PANALYTICAL Co.).

3. Results and Discussion

3.1 Chemical analysis of limestone

All the limestone samples belonged to high quality class with more than 52 wt.% \( \text{CaO} \) content and the content of impurities was relatively similar. Chemical components of the eight limestone samples were analyzed using XRF as shown in Table 1. Belize limestone samples from the Cenozoic era had high \( \text{CaO} \) content of 54.58–55.24 wt.%, and limestone samples of Japan belonging to the Mesozoic era contained high \( \text{CaO} \) corresponding to 54.55–54.59 wt.%. In addition, South Korean limestone samples from the late Paleozoic era had 53.53–53.7 wt.% of \( \text{CaO} \). The other samples from the early Paleozoic era contained 51.51–51.97 wt.% of \( \text{CaO} \) and it was shown that the content of \( \text{CaO} \) increased in accordance with the formation age. However, because it was affected by variables such as mining location and peripheral deposits around the limestone ore, the content of \( \text{CaO} \) was not constant. Hence, there was a limit to derive a clear linear relationship between the \( \text{CaO} \) content and the formation age.

3.2 The relation between calcite twins and formation age

In this study, in order to investigate the influence of the presence of calcite twins together with the formation ages of limestone on the hydraulic activity of quicklime, a polarizing microscope analysis of thin sections of limestone was performed. Fig. 3 presents the results of the polarizing microscopy analysis including two Cenozoic, early Paleozoic, and late Paleozoic samples.

Fine-grained calcite crystals were shown in samples from the Cenozoic era. Otherwise, coarse-grained calcite crystals were detected in samples from the Paleozoic era such as LP-2 and EP-2. Also, calcite twins and cleavage were recognized well in LP-2 and EP-2. From the experiment, it is revealed that the aged limestone had bigger calcite crystals and more calcite twins were displayed often.

To determine a high stress field of limestone ore, the existence of calcite twins is examined. Because the presence of calcite twins indicates the temperature at the time when limestone deposits generated and the direction of the high stress fields is indicated by the location where calcite twins are observed. According to Park (2007), calcite twins were generated in the late Triassic, Jurassic, Daebog orogeny, and Cretaceous periods and generally formed at 200°C or less. Since it has been subjected to external stresses such as

| Table 1 | Chemical components (wt.%) of the limestone ore samples analyzed using X-ray fluorescence (XRF) |
|---------|--------------------------------------------------------------------------------------------------|
|         | \( \text{Al}_2 \text{O}_3 \) | \( \text{CaO} \) | \( \text{Fe}_2 \text{O}_3 \) | \( \text{K}_2 \text{O} \) | \( \text{MgO} \) | \( \text{MnO} \) | \( \text{Na}_2 \text{O} \) | \( \text{P}_2 \text{O}_5 \) | \( \text{SiO}_2 \) | \( \text{TiO}_2 \) | \( \text{L.O.I} \) |
| CE-1    | 0.12 | 54.58 | <0.01 | 0.09 | <0.01 | 0.3 | <0.01 | <0.01 | <0.01 | 0.79 | 0.02 | 43.46 |
| CE-2    | 0.3 | 55.24 | 0.11 | <0.01 | 0.01 | 0.45 | 0.01 | 0.02 | <0.01 | 0.85 | 0.01 | 42.6 |
| ME-1    | 0.06 | 54.59 | <0.01 | 0.02 | 0.43 | <0.01 | 0.01 | 0.02 | <0.01 | 0.38 | <0.01 | 43.9 |
| ME-2    | <0.01 | 54.55 | <0.01 | 0.01 | 0.41 | <0.01 | 0.03 | <0.01 | 0.23 | <0.01 | 44.02 |
| LP-1    | 0.22 | 53.53 | 0.12 | 0.02 | 0.19 | <0.01 | 0.01 | 0.02 | 2.78 | 0.02 | 42.72 |
| LP-2    | 0.38 | 53.7 | 0.23 | 0.07 | 0.34 | <0.01 | 0.02 | <0.01 | 2.22 | 0.02 | 42.87 |
| EP-1    | 0.01 | 51.97 | 0.04 | 0.01 | 0.25 | 0.02 | 0.02 | <0.01 | 6.02 | <0.01 | 41.25 |
| EP-2    | 0.89 | 51.51 | 0.29 | 0.32 | 1.43 | <0.01 | <0.01 | 0.02 | 3.04 | 0.05 | 42.35 |

– CE: The Cenozoic Era (about 0.6 million years ago)
– ME: The Mesozoic Era (about 2.2 million years ago)
– LP: The Late Paleozoic Era (about 3 million years ago)
– EP: The Early Paleozoic Era (about 5 million years ago)
Comparing the hydraulic activity of limestone with its formation age, the temperature change of EP was about 10°C. It means the temperature increases only about 10°C after hydration starts. The range of the hydraulic activity of LP and ME is relatively wide and the average change of temperature was 17°C and 23°C, respectively. But their values are higher than that of EP. For CE, the temperature rises to about 60°C after the start of hydration and shows the highest hydraulic activity among the chronological limestone groups. That is, the hydraulic activity of the recently formed limestone such as sample CE is higher than that of past samples, because the temperature increases quickly after the start of hydration.

Hogwoning (2006) refers that the existence of calcite twins in limestone causes specific thermo-dynamic interactions during calcinations which are abetting the sintering process and reduces the hydraulic activity of limestone. As results shown in Fig. 4, the aged limestones which display calcite twins have small surface area to react with water, showing low hydraulic activity. Otherwise, the newer limestones have large surface area and reacted with water more efficiently, showing high hydraulic activity.

### 3.4 Yield of aragonite with formation age of limestone

The production yield of aragonite was calculated by Rietveld method and the results are shown in Fig. 5 and Fig. 6. Eight samples from different formation ages did not produce pure aragonite PCC. However, the yield of aragonite PCC tended to depend on the formation age of limestone. It was confirmed that the yield of aragonite PCC increased with the use of recently generated lime-

---

**Fig. 3** Polarizing microscopy: 1) CE-2, 2) LP-2, 3) EP-2 (X40. Cross N. 0.5 cm = 100 μm, Cc = calcite)

---

**Fig. 4** Variation of hydraulic activity with formation age of limestone

---

...
stone such as CE.

The diagram shown in Fig. 6 is corresponding with the research of Kim (2007). It reports that if the initial hydration temperature gets higher, the particle size of calcium hydroxide and the production yield of aragonite PCC will increase\textsuperscript{9,10}. For that reason, the initial temperature in this study was fixed at 25°C. Consequently, we could consider the effect of hydraulic activity with the influence of formation age on the hydration and the production yield of aragonite PCC only. As shown in Fig. 5 and Fig. 6, it has found that recently generated limestone has a high hydraulic activity and as a result the initial temperature of hydration increases sharply. The preparation of calcium hydroxide in large particle size thus becomes possible, and eventually, the production yield of aragonite can be increased.

4. Conclusions

This study investigates the effects of geological

![Fig. 5 The yield of aragonite and calcite PCC by Rietveld method](image)
properties of limestone on the hydraulic activity and the synthetic characteristics of aragonite PCC by using eight limestone samples having different formation ages. The results show that the hydraulic activity of limestone and the production yield of aragonite increase as the formation age of limestone increases. Briefly, as limestone is aged, it has lower hydraulic activity and produces more calcite than aragonite when synthesizing. Furthermore, the existence of calcite twins is related to the formation age.

The foregoing analysis has demonstrated the validity of the hypothesis that the formation age of limestone has a major impact on the hydraulic activity, chemical components of limestone samples and calcite twins. In recent years, numerous studies have attempted to find the factors affecting hydraulic activity and the synthesis of PCC. However, the fundamental importance of the origin and formation age of limestone has been examined.

Fig. 6  Variation of yield of aragonite with formation age of limestone

Acknowledgment

This research was supported by a grant (2013) from the Energy Technology Development Program (2013T100100021) funded by the Ministry of Trade, Industrial and Energy of the Korean government.

References

1. B.J. Jung and Y.J. Park: Calcination mechanism of limestone: Journal of Korea institute Che. Eng., 24(3), pp. 203–213 (1985)
2. Robert, S. Boynton: Chemistry and Technology of lime and limestone (1966)
3. Korea Resources Corporation: A general survey of a mining industry in Korea, Report (2010)
4. S. Hogewoning: The relation between limestone properties and quicklime reactivity, 11th International Lime Association (2006)
5. Gischlera, J. Harold Hudson: Holocene development of the Belize Barrier Reef, Sedimentary Geology, 164, pp. 223–236 (2004)
6. Korean Standard (KS E 3077): Testing method for hydraulic activity of limestone used to precipitated calcium carbonate, 71.040.40 (2006)
7. J.H. Kim, J.W. Ahn, H.S. Park, C.H. Park: Synthesis Peculiarity of the Precipitated Calcium Carbonate Polymorphs Following Variation of Supersaturation in Ca(OH)2 and Na2CO3 Reaction System, Journal of the Korean Society for Geosystem Engineering, 7(4), pp. 95–102 (2004)
8. Y.S. Park, B.A. Jang, J.B. Kim, S.S. Kang: Analysis of Calcite Twins as Indicators of Paleostress History, Econ. Environ. Geol., 40(4), pp. 461–471 (2007)
9. J.A. Kim, J.W. Ahn, K.S. You, H. Kim, H.C. Cho, I.C. Lee: The effect of initial hydration temperature on the characteristics of calcium hydroxide and aragonite precipitated calcium carbonate, Solid state phenomena Vols. 124–126, pp. 815–818 (2007)
10. J.A. Kim, G.C. Han, M.H. Lim, K.S. You, M.Y. Ryu, J.W. Ahn, T. Fujita, H. Kim: Effect of hydraulic activity on crystallization of precipitated calcium carbonate (PCC) for eco-friendly paper, Int. J. Mol. Sci., 10, pp. 4954–4962 (2009)