

Manufacture of Aragonite Precipitate Calcium Carbonate by a Carbonation Process Using Dusts from a Stainless Steel Refining Sludge Plant in POSCO

J.W. Ahn*, H.S. Kim, H. Kim^a, S.H. Yoon^a, J.S. Kim^b and G.W. Sung^b

Minerals & Materials Processing Division, Korea Institute of Geoscience & Mineral Resources, Taejeon 305-350, Korea

^aSchool of Materials Science & Engineering, Seoul National University, Seoul 151-742, Korea

^bPOSCO, Pohang, 790-785, Korea

The conditions for the synthesis of aragonite by a carbonation process were investigated, and these results were applied to the recycling of dusts generated from a steel works. The formation of aragonite has no relation with the pH value, the molar ratio of $\text{MgCl}_2/\text{Ca}(\text{OH})_2$, and Mg/Ca ion concentration in the solution. The condition for the synthesis of aragonite requires that the concentration of Mg ions should be in the appropriate range (about 0.1~0.26 mol/L), and the concentration of Ca ions below a certain range (about 0.25 mol/L). Too much Ca ions or Mg ions favor the formation of calcite. Needlelike aragonite was successively synthesized using dusts, and thus effective recycling of dusts can be expected.

Key words: CaCO_3 , aragonite, carbonation process, recycling, dusts.

Introduction

There are three polymorphisms of calcium carbonate and these are calcite, aragonite and vaterite. Among these materials, calcite is the only stable phase at room temperature and pressure, which is easily synthesized and generally used. Aragonite and vaterite are meta-stable phases under natural conditions and thus difficult to synthesize. Recently, needlelike aragonite with its high aspect ratio is desired for many applications such as improvement of the mechanical properties of polymer and rubber materials, or reinforcing materials in the paper industry.

It is generally known that Mg ions inhibit the growth of calcite and thus enhance relatively the formation of aragonite in the precipitation of calcium carbonate in solution. There are many reports about the effects of Mg ions on the phase formation and crystal growth of calcium carbonate [1-5]. The aragonite can be synthesized using these effects. The crystal can be prepared either by the reaction of solutions containing calcium ions and carbonate ions, or by the carbonation process in which $\text{CO}_2(\text{g})$ is blown into a $\text{Ca}(\text{OH})_2$ slurry. In the case of the former, aragonite can be obtained easily only if the reported conditions of the synthesis are met. But in case of the latter, the reports are insufficient, and further each reported set of experimental conditions about the synthesis of aragonite are different and somewhat inconsistent [4-5].

Ota *et al.* [4] reported that aragonite can be synthesized by blowing CO_2 gas into the mixture of $\text{Ca}(\text{OH})_2$ slurry and MgCl_2 solution, with an initial pH value of 9 at 80°C . They emphasized that the initial pH value of the reaction mixture solution determines the formation of aragonite. But in our experiment, if total amount of batch or starting materials varied, the precipitated phase was aragonite in one case or calcite in the other although the initial pH values were the same. Thus we cannot conclude that the initial pH value of the mixture solution necessarily determines the formation of aragonite. Sasaki *et al.* [5] reported that the important factors to obtain aragonite were the molar ratio of the starting materials MgCl_2/CaO , the flow rate of $\text{CO}_2(\text{g})$, the reaction time, the pH, and the reaction temperature. In the case of the mole ratio of MgCl_2/CaO , they mentioned that the aragonite phase was dominantly formed when the mole ratio of MgCl_2/CaO was 1.6 under the conditions of 35°C and a $\text{CO}_2(\text{g})$ flow rate of $50 \text{ cm}^3/\text{min}$. But in their data, the major phase was different for each case when the amount of starting material CaO was 5 g and 20 g, although the molar ratio of MgCl_2/CaO was 1.6. Thus the value of the molar ratio of the starting materials cannot necessary define the condition of the formation of aragonite.

Considering these points, the suggested conditions for the synthesis of aragonite can be applied only to the their specific reaction system and thus cannot be applied perfectly if the amount of the batch or the starting materials changes. So it is necessary to find the synthesis conditions which are consistent and generally applicable irrespective of the amount of the batch.

In this study we intended to define the conditions for

*Corresponding author:
Tel : +82-42-868-3578
Fax : +82-42-861-0861
E-mail: ahnjw@rock25t.kigam.re.kr

the synthesis of aragonite which are generally applicable to any reaction system, and to apply these results in the recycling area. Annually a large quantity of dust of which the major compositions are a CaO-Ca(OH)₂ type mixture, are generated from steel works. For example, the amount of dust from a Korean steel company named POSCO (Pohang Iron & Steel Co., Ltd) is 6 tons/day, and this dust is not reused effectively yet. For the recycling of dust, synthesis of calcium carbonate can be considered, and it would be far better if high value added-aragonite can be obtained. Thus, in this study we explore the conditions for the synthesis of aragonite and the application to dust.

Experimental Procedures

In the experiments for defining the synthesis condition of aragonite, the starting materials are reagent grade Ca(OH)₂ and MgCl₂. Ca(OH)₂ slurry was added to MgCl₂ aqueous solution and the total volume of the reaction solution was fixed to 1 L. The amount of Ca(OH)₂ was varied in the range of 0.05-0.4 mol, and that of MgCl₂ was varied in the range which sets the pH value of the reaction solution from 11 to 7.5. The reaction temperature was 80°C or room temperature, and the CO₂(g) flow rate was fixed at 100 ml/min. The completion of the reaction was identified by observing the constancy after the decrease in the pH value, and the precipitates were sampled, washed and dried.

In this kind of experiment, we should be aware that all of the added MgCl₂ does not contribute to Mg²⁺ ion formation in the reaction solution and part of it exists in the form of Mg(OH)₂. And as the amount of MgCl₂ increases, the pH value of the reaction solution decreases, which accompanies the increase of Ca²⁺ ion due to enhanced Ca(OH)₂ dissolution. Thus, if the total amount of starting materials changes, the amount of Ca and Mg ions also change, although the pH value of the reaction solution is the same or the molar ratio of MgCl₂/Ca(OH)₂ is the same.

From these points, we can expect that the concentration of each ion or the ratio of them determines the formation of aragonite. Thus the concentration of Ca and Mg ions in the initial reaction solution was analyzed by ICP (Inductively Coupled Plasma Spectrometry), and the effect of the concentration or ratio of each ion on the phases formation was investigated. X-ray diffraction (XRD) analysis was performed to identify the crystalline phase, and morphologies were examined using scanning electron microscopy (SEM).

The induced conditions for the synthesis of aragonite were applied to CaO-Ca(OH)₂ type mixtures of dusts. The dusts used in this study are waste generated from steel works (POSCO) and the major compositions analyzed by XRF (X-Ray Fluorescence Spectrometry) are CaO (78.6 wt%), Fe₂O₃ (9.9 wt%), Al₂O₃ (6.4 wt%), SiO₂ (3.3 wt%) and MgO (1.8 wt%). These dusts were

Table 1. Experimental conditions and ion concentrations when the amount of Ca(OH)₂ is fixed to 0.2 mol

Batch number	Temp. (°C)	pH	Starting Materials (mol)		Ion concentration (mol/L)	
			Ca(OH) ₂	MgCl ₂	Ca	Mg
(1)	80	11.7	0.2	0	0.015	0
(2)	80	10.0	0.2	0.15	0.150	0.00016
(3)	80	9.0	0.2	0.17	0.140	0.005
(4)	80	8.1	0.2	0.4	0.162	0.255
(5)	80	7.3	0.2	0.8	0.170	0.502
(6)	27	8.9	0.2	0.4	0.144	0.189
(7)	27	8.7	0.2	0.8	0.146	0.585
(8)	27	8.1	0.2	1.36	0.140	1.160

pre-treated with such processes as wet sieving, gravity separation and magnetic separation, and then the synthesis of aragonite was performed.

Results and Discussion

Table 1 shows experimental conditions and ion concentrations when the amount of Ca(OH)₂ is fixed to 0.2 mol and the pH value is adjusted by the amount of MgCl₂ in the total reaction solution of 1 L. The concentration of Ca ions increases about 10 times under the condition of the pH value at 10 as compared with the case of no MgCl₂ addition, and increases very slightly with the further decrease of the pH value. The concentration of Mg ions is very low compared with the amount of MgCl₂ under the condition of the pH value at 10. As the pH value decreases by the increase of the amount of MgCl₂, the concentration of Mg ions increases abruptly and becomes the same order as the amount of MgCl₂ in the case of the pH values of 8.1 and 7.3 at 80°C. When the amount of MgCl₂ is small, most of the Mg ions react with OH⁻ ions forming Mg(OH)₂, and this Mg(OH)₂ phase was identified by XRD data in our experiment. As the precipitation of CaCO₃ proceeds and is completed, the pH value of the reaction solution decreases, and this accompanies Mg(OH)₂ dissolution. As the amount of MgCl₂ increases, the portion of it which contribute to Mg ions in the solution increases.

Figure 1 shows XRD results corresponding to the experimental conditions in Table 1. At the reaction temperature of 80°C, the calcite is mainly formed at the pH values of 11.7, 10 and 9, and the aragonite is mainly formed at the pH value of 8.1. Ota *et al.* [4] reported that the aragonite was synthesized when the pH value of the reaction solution was 9, but in our study aragonite was synthesized at a pH value of 8.1 under the experimental conditions in Table 1, and thus some discrepancies exist between the two. In case of a pH value of 8.1, the ion concentrations of Ca and Mg in the reaction solution are 0.162 and 0.255 mol respectively, that is, the concentration of each ion is

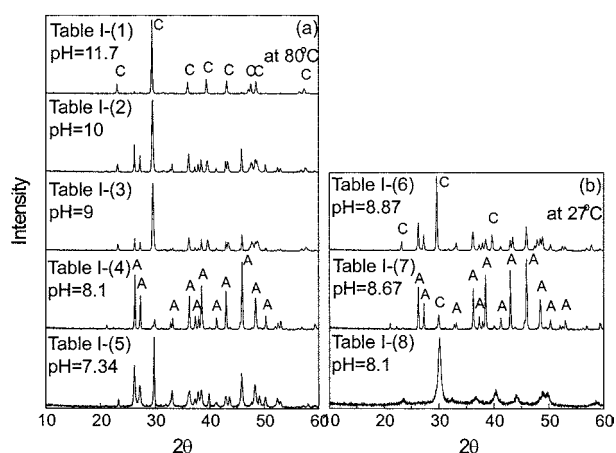


Fig. 1. XRD patterns of precipitated calcium carbonate at the reaction temperature of (a) 80°C, (b) room temperature for the experimental condition in Table 1.

similar compared with the case of the other pH value. It is generally known that Mg ions inhibit the growth of calcite and thus enhance relatively the formation of aragonite in the precipitation of calcium carbonate in solution.

However, we can notice that too high concentration of Mg ions, on the contrary, inhibits the formation of aragonite and enhances that of calcite in Fig. 1(a) and (b). Thus it seems that there are some ranges of the concentration of Mg ions in which the formation of aragonite is dominant. The reason why the formation of calcite is dominant under the conditions of too high as Mg ion concentration is not clear. But the main peak of calcite in case of Mg ion excess condition (Table 1-(5) in Fig. 1(a) and Table 1-(8) in Fig. 1(b), $2\theta = 29.80^\circ$ and 30.12° respectively) shifted to higher angles compared with that of Mg ion-deficient condition (Table 1-(1) in Fig. 1(a) and Table 1-(6) in Fig. 1(b), $2\theta = 29.40^\circ$ and 29.62° respectively). When the concentration of Mg ions is too high, Mg ions also precipitate with Ca ions forming a calcite structure $(\text{Ca}, \text{Mg})\text{CO}_3$ solid solution, and these precipitates become the major phase.

Then, in order to confirm whether the pH value of the reaction solution determines the formation of aragonite as mentioned by Ota *et al.* [4], experiments for the conditions in Table 2 were performed and XRD results are shown in Fig. 2. When the pH value is 9, the major precipitated phase is the calcite in all cases. When the pH value is 8.1, the major precipitated phase is the aragonite in the cases where the amount of $\text{Ca}(\text{OH})_2$ is 0.05 and 0.2 mol (Table 2-(4) and Table 2-(5)). But in the case where the amount of $\text{Ca}(\text{OH})_2$ is 0.4 mol (Table 2-(6)), the major precipitated phase is calcite although the pH value is 8.1. When the amount of $\text{Ca}(\text{OH})_2$ increased to 0.4 mol, the amount of MgCl_2 also increased to set the pH value to 8.1, but the amount of Mg ions, on contrast, decreased compared with the case where the amount of $\text{Ca}(\text{OH})_2$ is 0.2 mol.

Table 2. Experimental conditions and ion concentrations for the several fixed pH values

Batch number	Temp. (°C)	PH	Starting Materials (mol)		Ion concentration (mol/L)	
			$\text{Ca}(\text{OH})_2$	MgCl_2	Ca	Mg
(1)	80	9.0	0.05	0.05	0.035	0.0064
(2)	80	9.0	0.12	0.17	0.13	0.0051
(3)	80	9.0	0.4	0.35	0.3	0.0022
(4)	80	8.1	0.05	0.15	0.035	0.115
(5)	80	8.1	0.2	0.40	0.162	0.255
(6)	80	8.1	0.4	0.48	0.253	0.079
(7)	80	7.7	0.4	0.6	0.242	0.152
(8)	80	7.4	0.4	0.8	0.26	0.4

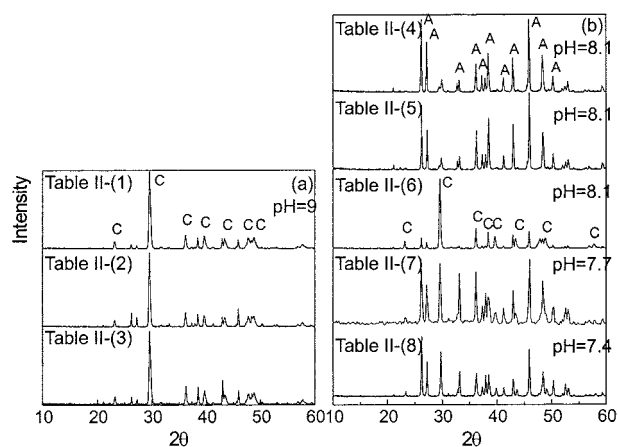


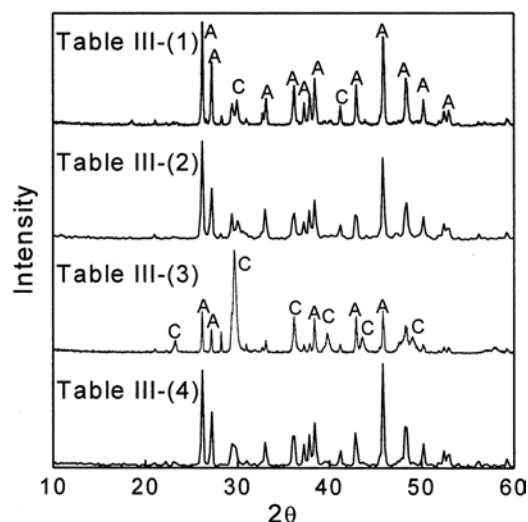
Fig. 2. XRD patterns of the precipitates when the pH value of the reaction solution is (a) 9, (b) below 8.1 under the experimental condition in Table 2.

Thus, although the pH value is same, the concentration of Ca and Mg ions or their ratio varies with changes in the amount of batch or starting materials, and this results in a difference in the phase of precipitates.

From these data (Table 2 and Fig. 2) several facts can be deduced. The formation of aragonite has no relation with the pH value from the data of Table 2-(4), Table 2-(5) and Table 2-(6). In addition, the molar ratio of $\text{MgCl}_2/\text{Ca}(\text{OH})_2$ cannot necessarily define the conditions for the aragonite formation because in spite of the same molar ratio of $\text{MgCl}_2/\text{Ca}(\text{OH})_2$, the results can be different from the data of Table 2-(5) and Table 2-(8). The molar ratio of Mg/Ca ion concentration in solution cannot also define the conditions for the aragonite formation because, the portion of aragonite phase is small although Mg/Ca ion concentration ratio is high from the data of Table 2-(5) and Table 2-(8). From the data in Table 1 and Fig. 1 we noticed that too high a concentration of Mg ions inhibited the formation of aragonite and enhanced that of calcite. From the data in Table 2 and Fig. 2, the condition of high Ca ion concentration in solution also favors the formation of calcite although Mg ion concentration is high (Table 2-(8)). Thus, the conditions for the synthesis of aragonite

Table 3. Experimental conditions in the case of using dusts

Batch number	Temp. (°C)	PH	Starting Materials (mol)		Ion concentration (mol/L)	
			Dust	MgCl ₂	Ca	Mg
(1)	80	8.1	0.05	0.12	0.023	0.088
(2)	80	8.01	0.05	0.17	0.026	0.13
(3)	80	8.1	0.2	0.23	0.1	0.009
(4)	80	7.94	0.2	0.4	0.1	0.15

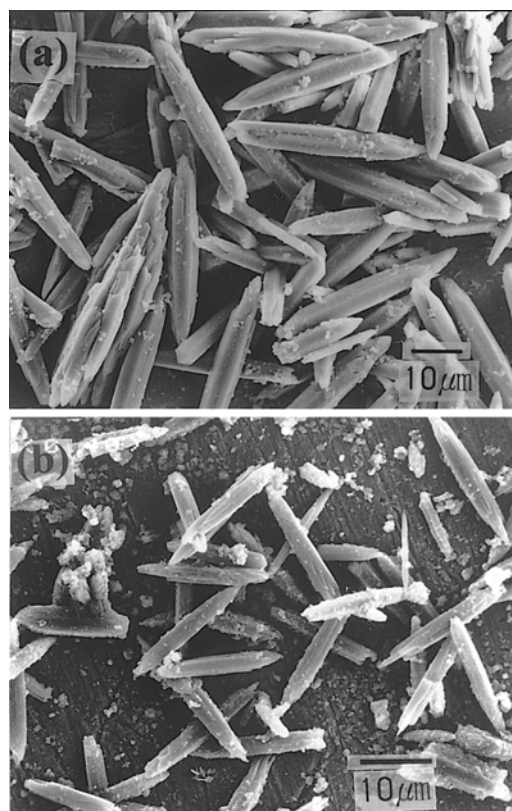
**Fig. 3.** XRD results of the precipitates when the starting materials are dusts under the experimental condition in Table 3.

requires that the concentration of Mg ions should be in the appropriate range (about 0.1~0.26 mol/L), and the concentration of Ca ions below a certain range (about 0.25 mol/L). Too high a concentration of Ca ions or Mg ions favors the formation of calcite.

Table 3 shows experimental conditions in the case of using dusts and the XRD results are shown in Figure 3. We can also confirm that the formation of aragonite has no relation with the pH value from Table 3-(1) and 3-(3) data, and the molar ratio of starting materials or Mg/Ca ion concentrations from Table 3-(1) and 3-(4) data, because the portion of aragonite is slightly higher, although the molar ratio of MgCl₂/Dust or Mg/Ca ion concentration is lower in the case of Table 3-(4) than that of Table 3-(1). Figure 4 shows morphologies of aragonite precipitated under the conditions in Table 1-(4) and Table 3-(4). Needlelike precipitates with a high aspect ratio can be obtained.

Conclusions

The conditions for the synthesis of aragonite were investigated. The formation of aragonite has no relation

**Fig. 4.** SEM photographs of the aragonite for the condition (a) in Table 1-(4): the starting materials are reagent grade Ca(OH)₂, and (b) in Table 3-(4): the starting materials are dusts

with the pH value, the molar ratio of MgCl₂/Ca(OH)₂ and Mg/Ca ion concentrations in the reaction solution. The conditions for the synthesis of aragonite requires that the concentration of Mg ion should be in the appropriate range (about 0.1~0.26 mol/L), and the concentration of Ca ion below a certain range (about 0.25 mol/L). Too high a concentration of Ca ion or Mg ions favors the formation of calcite. These results were applied to dust and needlelike aragonite was successfully synthesized, and thus effective recycling of dust can be expected.

References

1. Bischoff, J.L., J. Geophysical Research 73[10] (1968) 3315-3322.
2. Nancollas, G.H. and Sawada, K., J. Pet. Technol. (1982) 645-652.
3. Gutjahr, A., Dabringhaus, H. and Lacmann, R., J. Cryst. Growth 158 (1996) 310-315.
4. Ota, Y., Inui, S., Iwashita, T., Kasuga, T. and Abe, Y., J. Am. Ceram. Soc. 78[7] (1995). 1983-1984
5. Sasaki, K., Hongo, M. and Tsunekawa, M., Shigen-to-Sozai 114 (1998) 715-720.