International Journal of Advanced Culture Technology Vol.10 No.1 284-293 (2022)
DOI https://doi.org/10.17703/IJACT.2022.10.1.284

IJACT 22-3-35

A Study on the Preparation of Precipitated Calcium Carbonate from Steelmaking Slag

Byung-Hyun, Shon

Professor, Dept. of Environmental Engineering, Hanseo University, 46, Hanseo 1-ro, Haemi-Myun, Seosan-Si, Chungcheongnam-do, Republic of Korea
bhshon@hanseo.ac.kr

Abstract

After extracting the calcium component from the KR slag and the converter slag using ammonium chloride solution, the extract was reacted with carbon dioxide to synthesize precipitated calcium carbonate (PCC). In order to understand the effect of ultrasonic waves on calcium extraction from slags and calcium carbonate synthesis, the efficiency of calcium carbonate synthesis according to the with or without of ultrasonic waves was analyzed. The synthetic efficiency of PCC was investigated according to various experimental conditions, and the synthesized calcium carbonate was analyzed using XRD and SEM. In both slags, the amount of PCC decreased as the reaction temperature increased. The pH at the end of the experiment capable of synthesizing the maximum PCC in the carbonation reaction was 7 (irradiated with ultrasound) and 8 (irradiated without ultrasound), respectively. Because the pH of the extraction filtrate is different when irradiated with or without ultrasound, the pH was adjusted to 9 by injecting an additive (10 M NaOH) before the carbonation experiment, and then the experiment was performed. When calcium was extracted from KR slag, the crystal phase appeared as calcite regardless of the pH at the end of the experiment. However, when calcium was extracted from the converter slag and the pH was set to 7 at the end of the experiment, the crystal phase of PCC appeared as a mixture of calcite and vaterite.

Keywords: *Calcium extraction, Calcite, Carbonation, Precipitated calcium carbonate(PCC), Slag*

1. INTRODUCTION

Steel production goes through complex processes such as iron making, steel making, continuous casting and rolling process, which not only uses a large amount of raw material s(iron ore and coal) and energy but also generates a lot of by-products and wastes [1]. The largest amount of these by-products is slag, which refers to the residue after extracting metal components in the process of manufacturing pig iron from iron ore [2]. Many studies have been conducted to utilize the blast furnace slag, which accounts for about 50% of the steel slag generation, and are currently being recycled in various ways such as cement admixtures, concrete admixtures, and concrete aggregates [2]. However, steelmaking slag is less active than blast furnace slag and cannot be used as a reactive material, and it is difficult to use as a material for concrete because of its instability against expansion and collapse [2].

Manuscript received: February 22, 2022 / revised: March 1, 2022 / accepted: March 8, 2022
Corresponding Author: bhshon@hanseo.ac.kr
Tel: +82-41-660-1368, Fax: +82-41-660-1368
Professor, Dept. of Environmental Engineering, Hanseo Univ., Korea

Raw materials that can react with CO_2 to synthesize carbonated materials include natural minerals containing alkaline earth metals (Ca or Mg) and industrial by-products containing large amounts of calcium. Steel slag, a representative industrial by-product containing calcium, can be divided into blast furnace slag generated in the iron making process and steel slag generated in the steelmaking process [3]. The advantage of slag in the mineral carbonation field is that it is cheaper than other primary minerals and is chemically unstable, so carbonation reactions with carbon dioxide are possible with little energy use, and the calcium content required for the carbonation reaction is high [4]. The amount of slag generated in Korea in 2013 was $2{,}430 \times 10^4$ tons/yr, and the largest amount of slag was blast furnace slag, which was $1{,}400 \times 10^4$ tons/yr [3].

In general, ultrasonic waves are known as a useful technique to increase the reaction rate as an effective stirring method in various chemical processes and to control the crystal form of the product during the mineral carbonation process using carbon dioxide. Irradiating ultrasonic waves on a liquid generate a fine airwave via cavitation to affect the crushing, dispersion, emulsification, and activation of reaction, etc [5].

Calcium carbonate ($CaCO_3$) is divided into precipitated calcium carbonate (PCC) synthesized through chemical precipitation and ground calcium carbonate (GCC) produced by physically crushing or crushing crystalline limestone. Hard calcium carbonate and ground calcium carbonate are not uniform in particle shape or size, but PCC is produced by a chemical reaction, so the particle shape and size are very regular. In the past, heavy calcium carbonate was mostly used in industrial sites, but in recent years, PCC is gradually replacing the demand [4]. Calcium carbonate is classified into three types according to its crystal structure, calcite, vaterite and aragonite, each of which is homogeneous. Calcite, which has hexagonal crystals, is thermodynamically stable and is most widely used in the industry, and vaterite is the most unstable spherical crystal and is easily transformed into calcite or aragonite [6].

In this paper, the optimal calcium extraction conditions from slags generated in the steelmaking process using ultrasonic waves, and various factors and conditions that influence the production of PCC by reacting the extracted calcium components and carbon dioxide are experimentally investigated.

2. THEORETICAL CONSIDERATION

2.1 Steel slag

The converter slag discharged from the steelmaking process is mainly composed of CaO and Ca_2SiO_4. The Ca_3SiO_5 is stable at a high temperature of 1,250～2,070℃, but when it reaches 1,250℃ or less through the cooling process, a part of Ca_3SiO_5 precipitates as free CaO through the decomposition reaction process as shown in reaction eq. (1) [7].

$$Ca_3SiO_5 \rightarrow Ca_2SiO_4 + CaO \quad (1)$$

The steelmaking process is divided into the pretreatment of hot iron, converter process, and secondary refining. Steelmaking slag is mainly composed of SiO_2 and CaO, and other heavy metals are also included.

Molten iron pretreatment process (KR slag): The molten iron preliminary treatment technology is a molten iron desulfurization technique that removes some of the sulfur components contained in the molten iron before the converter process [8]. The impurities contained in the molten iron are classified by the characteristics of the impurities and then removed in a process having a relatively low refining cost. In addition, impurities that are difficult to remove sufficiently in a particular unit process may be sequentially refined in various processes to reduce the load of any particular process. By applying this technology, the efficiency, productivity and economics of the refining process can be improved simultaneously. The slag discharged after removing sulfur

and phosphorus in the molten iron preliminary treatment process is called molten iron preliminary slag.

Converter steelmaking process (Converter slag): The converter steelmaking process determines the basic quality of steel by pouring molten iron into the converter and injecting high-purity oxygen at high pressure to burn carbon and reduce impurities. Resources such as metal and iron in the converter slag are recovered and used for iron ore, scrap and limestone. Converter slag has the limitation that it cannot be recycled to concrete aggregate because of instability of expansion collapse by free CaO [9]. Converter slag is mostly recycled as a raw material for cement, but it is likely to be used as other high value added materials. The converter uses more than 99.5% high-purity oxygen, so the nitrogen content in the steel is lower than that of steel produced in ordinary furnaces. In addition, since the oxygen contact temperature is 2,000 to 3,000°C., slag formation by lime proceeds quickly, and decarbonization and dephosphorization are performed in parallel, so that steel having a low phosphorus and oxygen content can be produced at all times

2.2 Ca extraction from slag

Many studies have been conducted to extract calcium from steelmaking slag using nitric acid, sulfuric acid and acetic acid. These acids have good calcium extraction efficiency, but have disadvantages such as low pH buffering ability, high solvent regeneration energy, and high material cost.

Hall et al. (2014) used ammonium compounds (NH_4Cl, NH_4NO_3) for the first time to extract calcium from steelmaking slag. Although ammonium compounds are less efficient in calcium extraction than acids, it has been reported to be more economical and efficient in the carbonation process [10]. In order to selectively extract the calcium component from the steelmaking slag, the calcium compound may be extracted by reacting the ammonium compound with the slag, and then calcium recovered as the PCC by injecting CO_2 gas [10].

$$2CaOSiO_2(a) + 4NH_4Cl(aq) \rightarrow 2CaCl_2(aq) + 4NH_3 + 2H_2O(l) + SiO_2(s) \quad (2)$$

$$2CaCl_2(aq) + 4NH_3(aq) + 2Cl_2 + 2H_2O \rightarrow 2CaCO_3(a) + 4NH_4Cl(aq) \quad (3)$$

2.3 Calcium carbonate synthesis

Carbonation method: Carbonation is a method of absorbing carbon dioxide into an aqueous calcium hydroxide solution. Currently, most of the industrial processes use carbonation method [11]. Among the methods of synthesizing calcium carbonate, the most inexpensive and commonly used method is carbonation. Carbonation is a method of precipitating calcium carbonate by mixing calcium hydroxide or calcium oxide with water, ethanol and methanol and then blowing carbon dioxide [12].

$$CO_2(g) \rightarrow CO_2(l) \text{ (Solvation)} \quad (4)$$

$$CO_2(l) + H_2O(l) \rightarrow H_2CO_3(l) \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \text{ (Reaction)} \quad (5)$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)\uparrow \triangle H(1000°C)=165.54 \text{ kJ/mol (Calcination)} \quad (6)$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \triangle H(35°C)=-65.47 \text{ kJ/mol (Hydration)} \quad (7)$$

$$Ca(OH)_2(s) \rightarrow Ca^{2+} + 2OH^- \text{ (Ionization)} \quad (8)$$

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \triangle H(45°C)=-112.48 \text{ kJ/mol (Carbonation)} \quad (9)$$

Aqueous solution method: Calcium carbonate is prepared by reacting an aqueous solution of calcium chloride, a by-product of the ammonium soda process, with an aqueous solution of ammonium carbonate or soda ash [13].

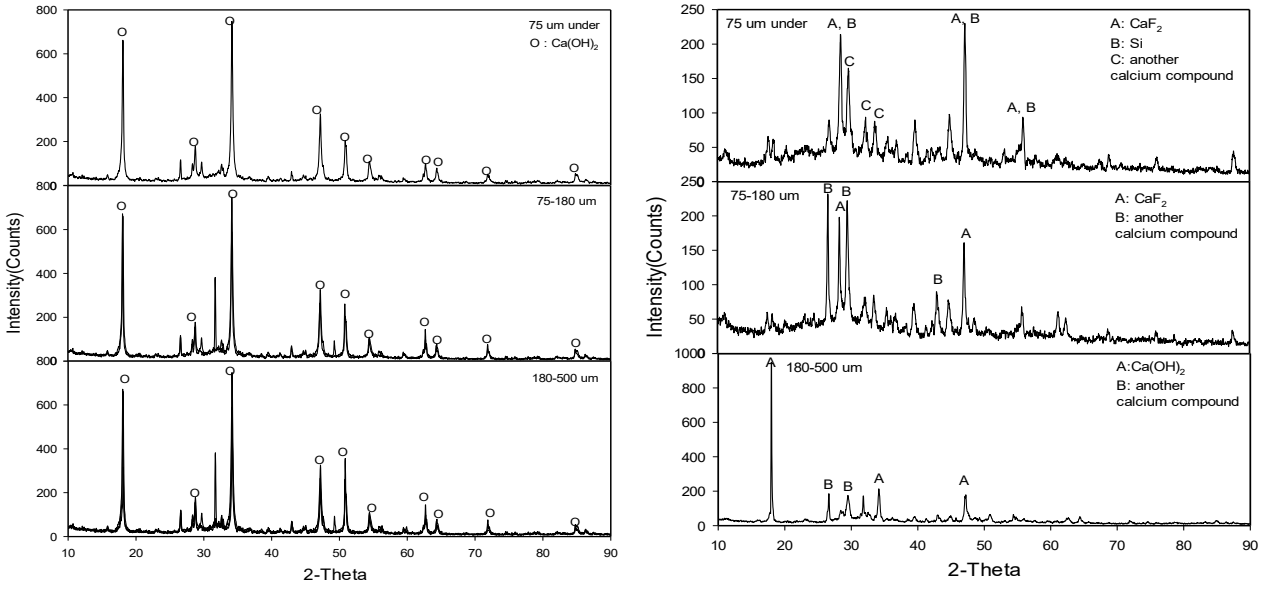
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl \quad (10)$$

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl \quad (11)$$

3. EXPERIMENTS

3.1 Sample

During the steelmaking process, impurities are discharged in the form of slag. Various components such as Ca, Si, and other heavy metals are mixed in this steelmaking slag, and it is often used as an aggregate of some concrete or a simple landfill material. In this study, KR and converter slags were used for the experiment. As a result of EDX analysis, the amount of Ca in the slag increased as the particle size decreased, and the KR slag was higher than that of the converter slag. As shown in Fig. 1, KR slag was mostly composed of $Ca(OH)_2$ and some impurities, and ($Ca(OH)_2$, other calcium compounds, CaF_2, and Si were detected in converter slag.



(KR slag) (Converter slag)

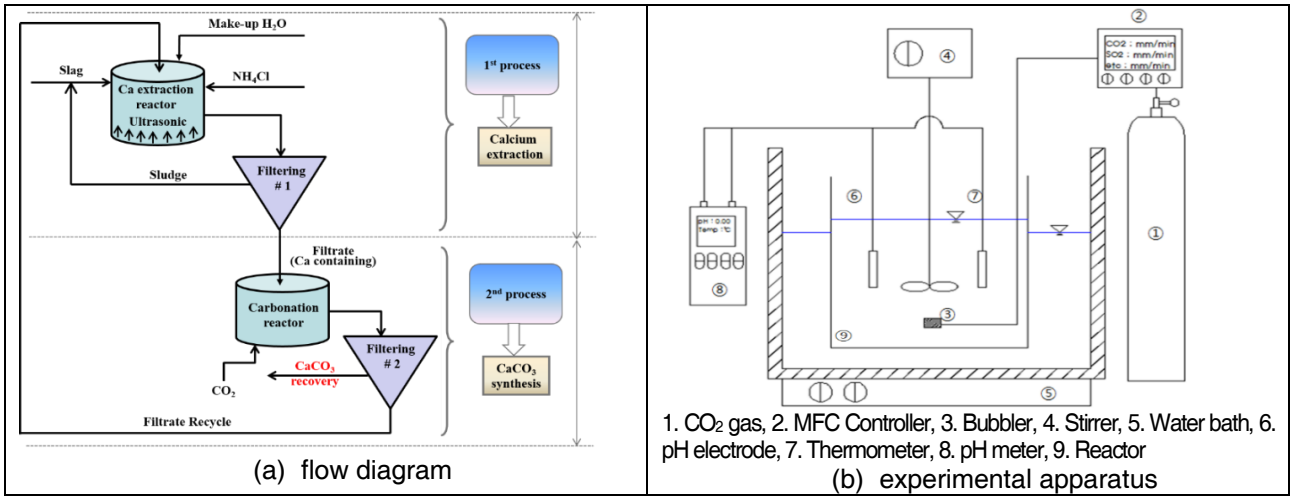
Figure 1. XRD diagram of raw slags

3.2 Method

As shown in Fig. 2(a), the experiment is divided into two processes: calcium extraction and calcium carbonate manufacturing process. The experimental apparatus and method for calcium extraction are detailed in the study of Hwang et al. [14]. When calcium extraction from the slag was completed, the filtrate and the extraction residue were separated using a vacuum filtration device. The extracted residue was dried in a drying oven for analysis and then stored in a desiccator, and the filtrate was transferred to a carbonation process and used to prepare PCC. The experimental apparatus for preparing PCC is shown in Fig. 2(b).

The experimental apparatus for manufacturing calcium carbonate is largely divided into a reactor and a carbon dioxide injection unit. A 1000 ml beaker made of a pyrex material was used as the reactor, and a water bath (Hanbaek Scientific, HB-205WS) was used to keep the temperature of the reactor constant. During the carbonation process, carbon dioxide was quantitatively injected at the bottom of the reactor from a CO_2 cylinder using an MFC controller (Lokas Automation, GMATE 2000), and a sparger was used to uniformly distribute CO_2 gas in the reactor. In the carbonation experiment, the generation of PCC is greatly affected by

pH, so after CO_2 injection, pH was continuously measured using a pH meter (Ecomeet, P15). When the carbonation reaction was completed, the generated PCC was recovered using a vacuum filtration device. The recovered PCC was dried at about 100°C in a drying oven and then weighed to analyze the recovery rate of PCC, and stored in a desiccator to analyze physical properties. The experimental variables in this experiment are reaction temperature, pH, and additives, and detailed experimental conditions are shown in Table 1.



(a) flow diagram (b) experimental apparatus

Figure 2. Process flow diagram and experimental apparatus

Table 1. Experimental variables and conditions

Variables	Conditions
Reaction temperature	30 40, 60
pH	6, 7, 8
Reaction time	Until the desired pH is reached
Stirring rate (rpm)	300
Flow rate of CO_2 (ml/min)	100
Additive	10 M NaOH

3.3 Analysis

When the carbonation experiment was completed, the difference in weight before and after the experiment was measured to determine the recovery rate of the PCC produced. The shape and particle size of the PCC were confirmed through SEM (Scanning Electron Microscope) photography and XRD analysis was performed to confirm the crystal phase.

4. RESULTS AND DISCUSSION

4.1 Ca extraction

For the two slags, the amount of calcium extraction was tested with and without ultrasonic irradiation. The optimal experimental conditions and extraction efficiency for calcium extraction are shown in Table 2 and are detailed in Hwang et al.[14]. Also, for convenience, the names for each experiment were defined as Ca extraction exp(1)-(4), and this calcium extract was used for PCC synthesis.

Table 2. Experimental conditions, extraction efficiency, and experiment name for Ca extraction

Slags	Ultrasonic irradiation	Experiment conditions	Ca extraction eff.(%)	Experiment name definition
KR slag	With	-. Particle size: 75 □m or less -. Reaction time: 2 hr. -. Reaction temperature: 60°C -. Extraction agent: 1 M of NH_4Cl	68.97%	Ca extraction exp(1)
	Without		61.44%	Ca extraction exp(2)
Converter slag	With		68.71%	Ca extraction exp(3)
	Without		49.70%	Ca extraction exp(4)

4.2 Effect of temperature on PCC synthesis

In the carbonation experiment, carbon dioxide was injected into the filtrate containing calcium, and the efficiency of producing PCC was investigated. The production efficiency of PCC according to the reaction temperature (30°C, 40°C, and 60°C) was investigated, and the experiment was terminated when the pH of the reactor reached 7. Fig. 3 shows the synthesis efficiency of PCC produced from KR slag and converter slag. In both slags, the amount of PCC synthesis decreased with increasing temperature. This is thought to be because the higher the temperature, the faster the reaction rate with CO2, so the pH changes too rapidly. In addition, it was found that the filtrate from which calcium was extracted by irradiation with ultrasonic waves produced less PCC than the filtrate that was not irradiated. It is thought that when ultrasonic waves are used, a lot of other components such as Mg and other components are extracted at the same time in addition to calcium contained in the slag, thereby acting as an interfering material in the formation of PCC.

In all cases, the time required to reach pH 7 in the carbonation reaction with the filtrate obtained by extracting calcium using ultrasonic waves was less than that in the case of extracting calcium without irradiation with ultrasonic waves. The filtrate from which calcium is extracted by irradiating ultrasonic waves has a lower pH than the case where ultrasonic waves are not irradiated and contains many impurities, and the reaction rate with CO2 is faster during carbonation. As a result, the synthesis efficiency of PCC is lower than that in the case of not irradiating ultrasonic waves because the pH drop rate is too fast and the synthesized PCC is decomposed and the Ca component is returned to the filtrate.

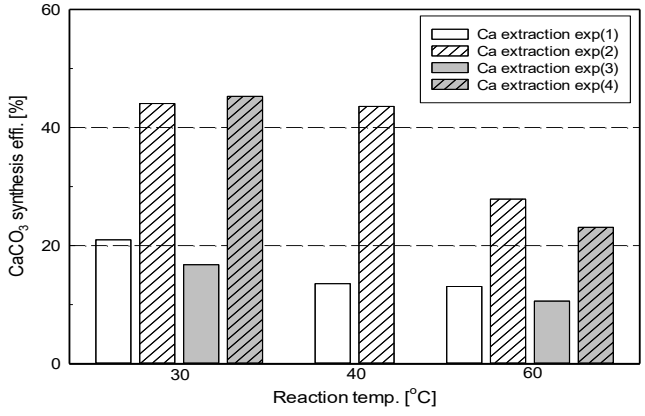
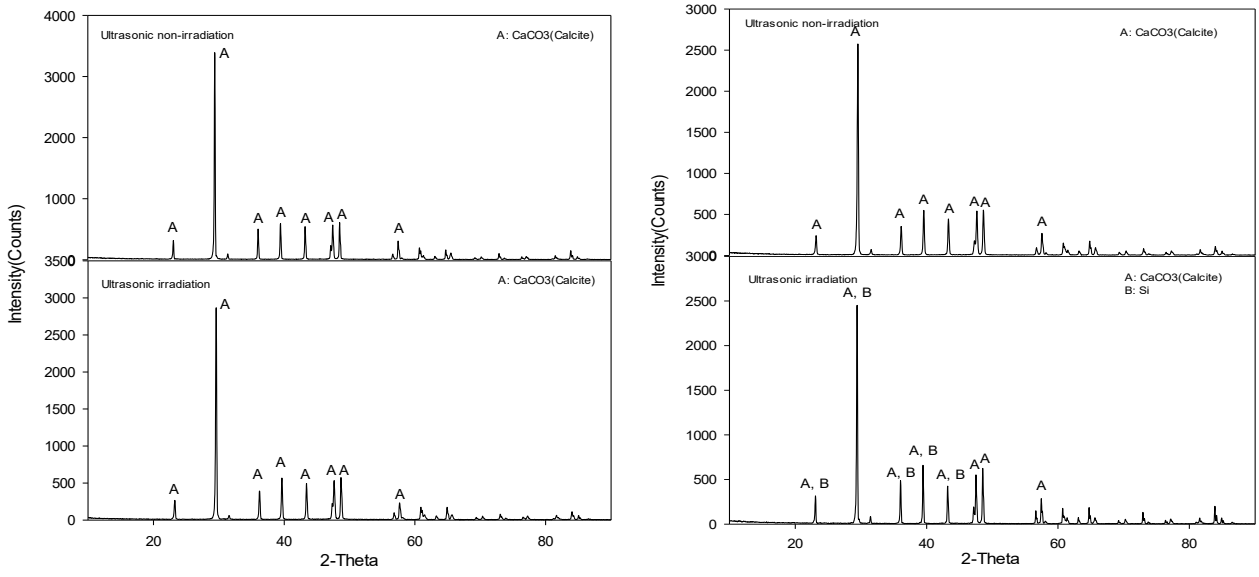


Figure 3. Calcium contents in raw KR and converter slags

Fig. 4 shows the XRD diagrams of PCC generated in the carbonation process of KR and converter slag, respectively. Whether irradiated with or without ultrasound, it can be seen that all are in the form of calcite.



(a) KR slag (b) Converter slag

Figure 4. XRD diagram of the PCC synthesized from the KR and converter slag

4.3 Effect of end pH on PCC synthesis

The PCC synthesis efficiency was measured while changing the final pH at a CO2 injection rate of 100 ml/min and a reaction temperature of 30°C. Fig. 5 shows the PCC synthesis efficiency according to the end pH change, and it was found that the PCC synthesis was affected by the end pH. When the filtrate extracted by irradiation with ultrasound was subjected to carbonation reaction, the PCC synthesis efficiency increased significantly as the pH increased, and the maximum PCC was produced at pH 8. This is thought to be because more calcium is extracted when extracted by ultrasonic irradiation, but PCC generated by the carbonation reaction is re-decomposed as the pH is lowered. However, when carbonation was performed with the extracted filtrate without ultrasonic irradiation, the pH was not significantly affected, and the maximum PCC was produced at pH 7. When calcium is extracted without irradiating ultrasonic waves, it is judged that more PCC is generated than when irradiated with ultrasonic waves because the pH of the filtrate is high.

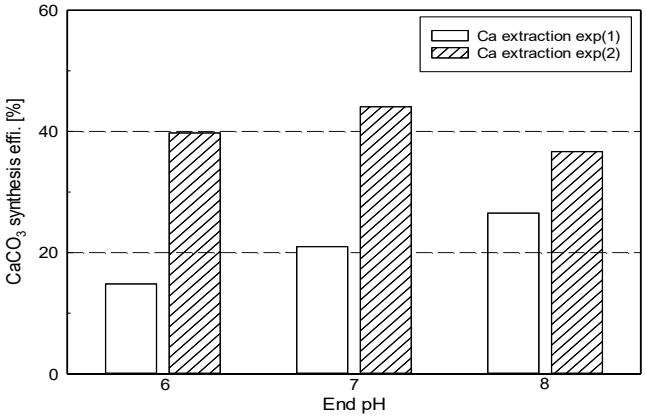


Figure 5. Effect of end pH on the synthesis of calcium carbonate from KR slag

Fig. 6 shows the SEM image of PCC prepared from KR slag. It was confirmed that calcium carbonate in the form of calcite was generated in both the case of using and not using the ultrasonic wave. In addition, calcite-type calcium carbonate was produced regardless of the final pH. As can be seen from the Fig. 6, when the final pH was 6, calcite-type calcium carbonate with a partially crushed shape was produced, but when the pH was 7 or higher, the hexagonal calcium carbonate having a perfect shape was produced.

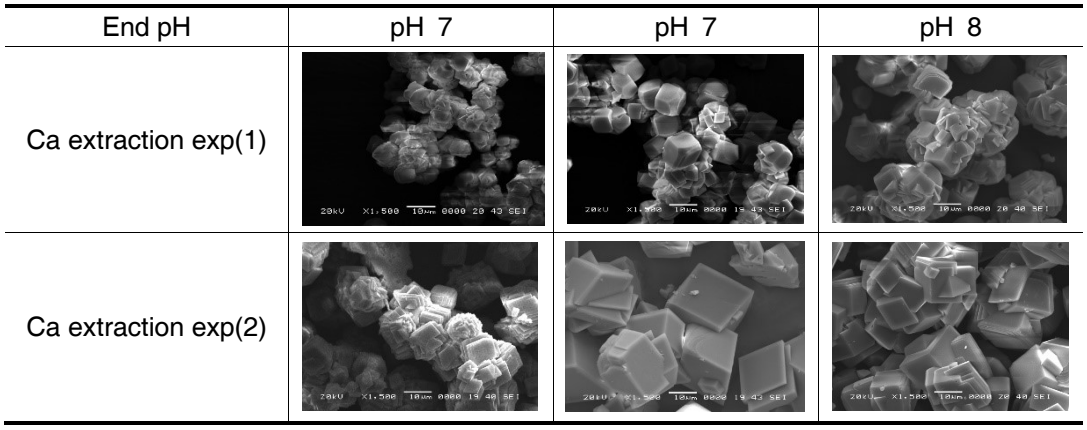


Figure 6. SEM photograph of PCC synthesized from the KR slag depending on the change in end pH

4.4 Effect of additives on PCC synthesis

As confirmed in the previous section, the amount of PCC produced from the filtrate obtained by extracting Ca using ultrasonic waves was about twice as low as that of the filtrate extracted without using ultrasonic waves. In order to find out the reason for this, the pH of the filtrate obtained by extracting Ca from the slag was adjusted to 9 using 10 M NaOH solution, and then the experiment was conducted. Fig. 7 shows the PCC synthesis efficiency according to the final pH during carbonation after adjusting the initial pH to 9 by injecting an additive (10 M NaOH). As shown in Fig. 7, compared with Fig. 5, it can be seen that the PCC synthesis efficiency is greatly increased. In particular, the PCC synthesis efficiency increased about 4 times and 2 times, respectively, when ultrasonic waves were irradiated and not irradiated. Regardless of the type of slag and the with or without of ultrasonic irradiation, the final pH showing the highest synthesis efficiency was 7.

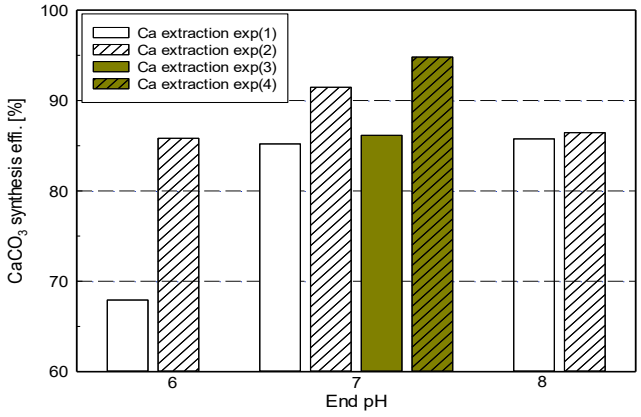
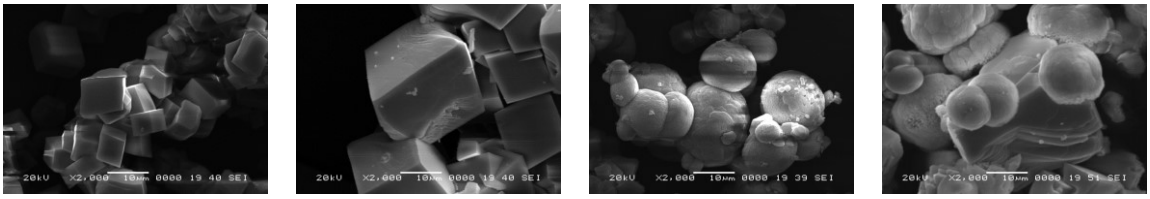


Figure 7. Effect of additives (10 M NaOH) on PCC synthesis efficiency

Fig. 8 shows SEM images of PCC prepared after injecting an additive into the filtrate extracted from two slags. In the case of KR slag, the crystal phase of PCC prepared by injecting additives, whether using ultrasonic waves or not, all showed a calcite form. In the case of converter slag, the crystal phase was found to coexist not only in calcite form but also in vaterite form of PCC. In particular, when calcium carbonate was prepared from the filtrate extracted from calcium using ultrasonic waves, the vaterite form was found to be prominent.



Ca extraction exp(1) Ca extraction exp(2) Ca extraction exp(3) Ca extraction exp(4)

Figure 8. SEM photograph of PCC synthesized from KR and converter slags after add of additives

5. CONCLUSION

Calcium was extracted from KR slag and converter slag using NH4Cl aqueous solution (with or without ultrasonic irradiation), and then the extracted filtrate was reacted with carbon dioxide to prepare calcium carbonate. As a result of the experiment, the following conclusions were obtained.

The optimal conditions for calcium extraction from KR slag and converter slag were a particle size of 75 μm or less, a reaction time of 2 hours, a reaction temperature of 60°C, and a concentration of 1M NH4Cl.

In both slags, the amount of PCC synthesis decreased as the temperature increased, and the filtrate extracted with ultrasonic waves produced less PCC than the filtrate extracted without ultrasonic wave irradiation.

When the filtrate extracted by irradiation with ultrasound was subjected to carbonation reaction, the PCC synthesis efficiency increased significantly as the pH increased, and the maximum PCC was produced at pH 8. However, when carbonation was performed with the extracted filtrate without ultrasonic irradiation, the pH was not significantly affected, and the maximum PCC was produced at pH 7.

After adjusting the pH of the calcium extraction filtrate to 9 by injecting an additive (10 M NaOH), regardless of the slag type and ultrasonic irradiation, the PCC synthesis efficiency was greatly improved by 2-4 times during carbonation (at the final pH of 7).

All crystalline phases of KR slag were in the form of calcite regardless of pH and ultrasound. However, in the case of converter slag, it was found that calcite and vaterite forms coexist regardless of ultrasonic waves when the end pH is 7.

ACKNOWLEDGEMENT

This research was supported by the research foundation from Hanseo University in 2019.

REFERENCES

[1] Chul-Kyu Choi, *Characteristics of livestock wastewater and high concentration waste water treatment using steelmaking slag*, Master Thesis, Andong National University, Andong, Korea, 2000.

[2] Eun-Ku Kwak, *A Study on the Application of Rapidly Cooling Steel Slag as Fine Aggregate for Concrete*, Ph.D. Thesis, Kongju National University, Kongju, Korea, 2011.

[3] Hyung-Sin Ahn, S*tudy on decision system on the economic evaluation of steel making slag aggregate*

utilizing, Master Thesis, Myongji University, Yongin, Korea, 2016.

[4] Arshe Said, "Enhancement of calcium dissolution from steel slag by ultrasound," *Chemical Engineering and Processing, Process Intensification*, Vol. 89, No. 3, pp. 1-8, 2015.

[5] Mason, T. J., "Practical sonochemistry," *Mineral Processing & Extractive Metall. Rev.*, Vol. 26, pp. 1-29, 2005.

[6] Kyung-Sun Song, Young-Nam Jang, Wonbaek Kim, Myung Gyu Lee, Dongbok Shin, Jun-Hwan Bang, Chi Wan Jeon, Soo Chen Chae, "Precipitated of calcium carbonate during direct aqueous carbonation of flue gas desulfurization gypsum," *Chemical Engineering Journal*, Vo. 213, pp. 251-258, 2012.

[7] Kyu-Don Moon, *A study on manufacturing process of the artificial aggregate by carbonation of the converter slag*, Master Thesis, Chungang University, Seoul, LKorea, 2001.

[8] Sang-Dong Lee, *Dephosphorization Behavior by Oxygen Potential Condition in Converter Pretreatment Process*", Master Thesis, Inha University, Incheon, Korea, 2008.

[9] Eun-Gu Kwak, *Utilization of Rapidly Cooled Steel Slag as Fine Aggregate for Concrete*, Ph.D. Thesis, Kongju Universit, Kongju, Koea, 2011.

[10] C. Hall, D.J. Large, "Calcium leaching from waste steelmaking slag- Significance of leachate chemistry and effects on slag grain mineralogy," *Minerals Engineering*, Vol 65, No. 15, pp. 156-162, 2014.

[11] Sung-Gyu Lyu, Gil-Soo Sur and Suk-Ho Kang, "A Study of Crystal of the Precipitated Calcium Carbonate Formed in the Emulsion State," *HWAHAK KONGHAK*, Vol. 35, No. 2, pp. 186-191, 1997.

[12] Se-Hoon Oh, A study on the recycling of waste gypsum, Master Thesis, Hanseo University, Seosan, Korea, 2017.

[13] Hye-Jin You, Morphology control of Calcium carbonate by adding Magnesium chloride, Master Thesis, SOON CHUN HYANG University, Cheonan, Korea, 2012.

[14] Min-Ho Hwang, Byung-Hyun Shon, "Effect of Ultrasonic Wave on Calcium Extraction from Steelmaking Slag," *International Journal of Emerging Technology and Advanced Engineering(IJETAE)*, Vol 8, Issue 8, pp. 220-227, August 2018.