Preparation of high-purity nano-CaCO$_3$ from steel slag

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ABSTRACT

Indirect carbonation is a suitable method for carbon dioxide (CO$_2$) removal from the environment, and it requires an acid to dissolve the calcium ions and a base to precipitate the formed calcium carbonate (CaCO$_3$). We herein report a new method to produce high-purity nano-CaCO$_3$ (nCaCO$_3$) from steel slag using hydrochloric acid (HCl) and sodium hydroxide (NaOH). The rate equation for the dissolution of calcium (Ca) in the slag was derived using a range of variables, such as temperatures, solid-to-liquid (S/L) ratio, and HCl concentration. The purified calcium hydroxide (Ca(OH)$_2$) was converted into nCaCO$_3$ (size: 80−120 nm, purity: 98.5%) by carbonation with CO$_2$, after impurities, such as iron (Fe), aluminum (Al), and Mg, were completely removed. An efficiency of 73% was obtained for the dissolution and precipitation steps when 0.50 M HCl and 1.0 M NaOH were employed to produce 1 ton/h of nano-CaCO$_3$ with a purity of 98.5 wt%. Recently, a sodium chloride (NaCl) electrolysis system with low energy requirement was proposed to simultaneously produce HCl and NaOH. Assuming 90% faradic efficiency in the aforementioned NaCl electrolysis, process energies of 916 kWh/tCaCO$_3$ and 1462 kWh/tCaCO$_3$ were obtained at potentials of 0.83 V and 1.50 V, respectively.

1. Introduction

Carbon dioxide (CO$_2$) is one of the main causes of global warming. Therefore, technologies for its emission reduction and removal are of particular interest. While replacing fossil fuels with renewable energy sources (e.g., bioenergy, solar energy, ocean energy, and wind energy) is a fundamental solution, carbon capture and storage (CCS) has been considered the most economically viable option for CO$_2$ disposal. Several key points of CO$_2$ capture have been identified to date, such as post-combustion, pre-combustion, oxy-fuel combustion, and industrial process streams. Furthermore, a number of options exist for the potential storage and utilization of CO$_2$, such as ocean disposal, saline aquifers, enhanced oil recovery, and depleted gas reservoirs. One particularly promising option for CO$_2$ fixing is storing it via mineral carbonation, i.e., the carbonation of natural silicate minerals, such as calcium and magnesium silicate, to produce mineral carbonates and silica [1,2].

$$(Ca, Mg)SiO_3 + CO_2 \rightarrow (Ca, Mg)CO_3 + SiO_2 \qquad (1)$$

It is the preferred method from the environmental aspect, as the mineralization products can store CO$_2$ for long periods of time [3,4]. Natural ores that contain alkaline earth metals, such as wollastonite (CaSiO$_3$), olivine ((Mg, Fe)$_2$SiO$_4$), and serpentine (Mg$_3$Si$_2$O$_5$(OH)$_4$), are typically selected as the feed stock for mineral carbonation. However, during the mining of such natural feedstocks, significant quantities of CO$_2$ are released. Therefore, alkaline industrial solid waste, such as steel slag, could be an alternative source of mineral carbonates [5]. Steel slag, which is a by-product obtained from the processing of steel and is composed of calcium, magnesium, aluminum, iron, and silicon-based compounds, is produced by treating impurities of iron ores with limestone [6]. The output of steel slag varies with the steel manufacturing process and the composition of limestone, and the average amount is ~0.2 ton for one ton of steel. Assuming the global demand for steel remains relatively constant, steel slag should be an excellent calcium source for use in CO$_2$ capture [7].

The carbonation of minerals using steel slag can be conducted by either direct carbonation or indirect carbonation methods. Direct carbonation involves treating solid steel slag with CO$_2$ in the gas phase or in aqueous solutions while indirect carbonation involves the extraction of alkaline mineral ions from steel slag and subsequent carbonation with gaseous- or aqueous-phase CO$_2$. One advantage of indirect carbonation is that it can produce pure

carbonates as a useful material, due to the selective extraction of reactive mineral ions (such as Ca and Mg ions) prior to carbonate precipitation [8]. Various acids, such as hydrochloric acid (HCl) [9], nitric acid (HNO₃) [2,10], and sulfuric acid (H₂SO₄) [2,11], have been employed to effectively extract alkaline earth metal ions from mineral ores. Meanwhile, bases are required for the production of calcium carbonate during carbonation. A mineralization scheme has been proposed to use HCl and MgCl₂/Mg(OH)Cl for extracting the alkaline earth metal ions and precipitating calcium carbonate, respectively [12]. During this process, HCl and MgCl₂/Mg(OH)Cl can be recovered and recycled. In addition, ammonium salts (e.g., NH₄Cl, NH₄NO₃) [13–15] and acetic acid (CH₃COOH) [6,16] have been investigated as reusable reagents for extracting metal ions for CO₂ removal.

Recently, electrolysis systems have been proposed for producing both HCl and NaOH at potentials <1.5 V in a single step, by modification of the chlor-alkali electrolysis process [17–20]. An electrodialysis method has also been proposed for the production of acids and bases for the mineralization of inorganic wastes [21]. Thus, assuming that a suitable electrochemical system to produce both HCl and NaOH exist, we propose coupling it to indirect carbonation to produce high-purity nano-CaCO₃ (nCaCO₃) from steel slag. The energy requirement of this novel process is also estimated.

2. Materials and methods

2.1. Dissolution of metal ions in steel slag

A round-bottomed flask (250 mL) equipped with a circulating water condenser was utilized for measuring the dissolution rate of slag in aqueous HCl solutions. The reactor was placed in a thermostatic water bath to control the dissolution temperature, and the HCl solution (250 mL, see below for concentrations) was heated to the desired dissolution temperature. While maintaining a constant reactor temperature, a measured amount of steel slag (<30 μm) was added to the reactor, and the resulting slurry was stirred at 400 rpm using a magnetic stirrer. A sample was then removed to calculate the Ca and Mg ion extraction rates. These samples were filtered rapidly using a 0.2 μm syringe filter (Whatman, PTFE), and the liquid filtrates were analyzed by ion-exchange chromatography (IC25A, Dionex) using an IonPac® CS12A cation-exchange column to measure the Ca and Mg ions concentrations in the sample. The dissolved fraction (x_i) of each element was calculated as follows:

$$x_i = C_i \times V/m_i \qquad (2)$$

Where, m_i (mg) is total amount of specific element i (Ca, Mg, Fe, Al, or K) in solid sample, C_i (mg/L) is concentration of dissolved specific element i in extracted solution and V (L) is volume of solution.

The variables affecting the dissolution rate are the solid/liquid (S/L) ratio, reaction temperature, and HCl solution concentration. The dissolution efficiency (%) was calculated by multiplying the dissolved fraction (x_i) by 100. To determine effect of HCl concentration on the extraction was examined using HCl concentrations of 0.50 M, 0.75 M, and 1.00 M at 30 °C, and an S/L ratio of 60 g/L. Dissolution experiments were conducted at 30 °C, 50 °C, and 70 °C using 0.50 M HCl and an S/L ratio of 50 g/L. In addition, the effect of the S/L ratio on the dissolution rate, slag/HCl solution ratios of 30 g/L, 40 g/L, 50 g/L, and 60 g/L were utilized.

2.2. Carbonation

After dissolving the steel slag in 0.50 M HCl with an S/L ratio of 50 g/L at 30 °C over 1 h, the solution was filtered (0.45 μm

Whatman filter paper) to remove the unreacted solid waste. Then, the metal ion concentrations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300, Perkin-Elmer, Inc.) prior to carbonation. Metal ions, such as Al, Fe, and Mg, were removed by titration with NaOH at either pH 7 or pH 11, and the removal efficiencies of the two pH values compared. Ca(OH)₂ slurries were prepared at pH 12.6 by the addition of 1 M NaOH to the resulting metal-free solution, and CO₂ gas was introduced into the slurries to give a pH of 8. The formed CaCO₃ was recovered by filtration (0.2 μm, Whatman filter paper), washed with triply distilled water, and dried under vacuum at 80 °C for 6 h.

2.3. Characterization

Scanning electron microscopy (SEM, S-5000H, Hitachi, Japan) and X-ray diffraction spectroscopy (XRD, XRD-6000, Shimadzu, Japan) were employed to determine the structural phase and morphology of the solid samples. XRD analysis was conducted in the continuous scan mode over a range of 10–80° under 40 kV/30 mA with CuK-α radiation. Elemental analysis of the solid samples was performed by ICP-OES and X-ray fluorescence (XRF, ZSX Primus II, Rigaku Corp. Japan). Surface area and pore size distribution measurements of the dried samples (raw and residual steel slag) were conducted by Brunauer–Emmett–Teller (BET) analysis (BELSORP-mini II, BEL Japan, Japan). Thermogravimetric analysis (TGA, DSC2010, TA Instruments, US) of the prepared CaCO₃ was performed to quantify the amount of CO₂ fixed in the solid samples, using a heating up to 950 °C at a rate of 10 °C/min under a flow of air at 100 mL/min.

3. Results and discussion

3.1. Dissolution of Ca and Mg ions in steel slag with HCl solution

Table 1 shows the XRF and ICP-OES compositional analysis of the steel slag from a blast furnace (POSCO, steel industry, Korea). Steel slag was composed of 47.0 wt% CaO and 31.5 wt% SiO₂, as well as minor amounts of Al₂O₃ (15.2 wt%), MgO (3.9 wt%), K₂O (0.5 wt%), and Fe₂O₃ (0.6 wt%). According to previous reports, steel slag was composed of CaO, SiO₂, MgO, Al₂O₃, and iron oxides [10]. In a basic oxygen furnace (BOF) and an electric arc furnace (EAF), the CaO content is generally within 34–50 wt% and 32–40 wt%, respectively. In addition, in these furnaces, Fe contents tend to be very high (15–30 wt%). Moreover, the Nippon blast furnace slag is composed of 41.7, 33.8, 7.4, and 0.4 wt% of CaO, SiO₂, MgO, and Fe₂O₃, respectively [22], which is comparable to the slag sample examined herein.

Figs. 1 and 2 show the effects of HCl concentration, dissolution temperature, and S/L ratio on the dissolution of Ca and Mg ions from the steel slag. Table 2 shows the dissolution efficiency of different metal ions under different dissolution conditions over 1 h. Pearson correlation coefficients for the linear dependency between each of these three variables and the dissolution efficiency are near either 1.0 or −1.0 (Table S1), indicating strong positive and negative relationships, respectively. The Pearson coefficient for the linear dependency between the S/L ratio and the dissolution efficiency of K is low (−0.639), but the negative dependency on the S/L ratio is clearly valid.

Figs. 1a) and 2a) show the effect of HCl concentration on the dissolution of Ca and Mg ions, respectively, at 30 °C with an S/L ratio of 60 g/L. The dissolution efficiencies of Ca ions at 0.50, 0.75, and 1.00 M HCl were 46%, 61%, and 76% after 20 min, respectively, while those of Mg were 32%, 48%, and 60%, respectively (Table 2). The dissolution efficiencies of both Ca and Mg ions in steel slag were 1.6