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Development of a new pH-swing CO_2 mineralization process with a recyclable reaction solution

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Abstract

A new CO_2 mineral sequestration process using the pH swing of a weak base–strong acid solution was proposed. In this process, an alkaline-earth metal was extracted selectively from silicate waste material, such as steelmaking slag or waste concrete, in an acidic condition using a weak base–strong acid solution. The reacted solution containing alkaline-earth metal ions and a weak-base, behaves as a CO_2 absorbent. The acidic extraction solution was regenerated from the basic absorbent solution by precipitating the alkaline-earth metal with CO_2 as the carbonate. The thermodynamic analysis of this process shows that a series of reactions proceeds spontaneously and the overall reaction is exothermic. The feasibility of the proposed process was confirmed using steelmaking slag as a silicate material and ammonium chloride solution as a weak base–strong acid solution. It was confirmed that this series of reaction proceeds successfully under mild conditions. Calcium ions were extracted selectively from steelmaking slag using an ammonium chloride solution, and the reacted solution absorbed CO_2 followed by the precipitation of $CaCO_3$ at 80 °C. On the basis of these experimental analyses, the energy consumption of the proposed process was roughly estimated as 300 kWh/ton-CO_2.
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1. Introduction

The increasing atmospheric concentration of CO_2 attributed to fossil fuel combustion is a serious problem leading to global warming. It is estimated that CO_2 emission by the year 2100 will be approximately four times larger than that in 2000 [1]. Therefore, a variety of options for reducing CO_2 emissions, such as fuel switching, exploitation of nuclear power or renewable energy, CO_2 capture and sequestration, planting, etc. have been extensively studied. Among them, CO_2 capture and sequestration, such as geological storage or ocean sequestration, have recently attracted considerable attention as one of the most promising practical options for reducing CO_2 emissions. However, the CO_2 capture and separation processes are energy consuming and are the main reasons for the high cost of the sequestration process. Therefore, the development of energy-saving and low cost CO_2 separation processes has been designed. On the other hand, mineral carbonation, which sequestrates CO_2 as a mineral carbonate, has recently attracted much interest because of its ability to sequestrate CO_2 indefinitely as chemically stable carbonates with a spontaneous and exothermic reaction, and hence has great potential to become economically feasible. In addition, mineral carbonation is also expected to offer an environmentally safe and permanent CO_2 disposal method [2]. However, since the weathering reaction of silicate materials containing alkaline-earth metal proceeds on a geological time scale, this reaction is not suitable for sequestration of CO_2 from the emission source on engineering time scales. Therefore, the

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development of a new system with a simple process, short reaction time and lower energy consumption are necessary for practical use. Many researchers have been investigating this process in order to solve the problem. For example, Lackner et al. [3], Moriyoshi et al. [4], Wu et al. [5], Kojima et al. [6], Fauth et al. [7], and Kakizawa et al. [8] focused on a rock weathering reaction and carried out mineralization studies of natural ore (wollastonite or forsterite). Fujii et al. [9] and Iizuka et al. [10] studied the mineralization processes using waste concrete as the alkaline earth metal source. A study of the production of a large block for use as an artificial reef for seaweed/fish by carbonating calcium from steelmaking slag [11] was also carried out. Some researchers succeeded in promoting the extraction reaction by using an extraction agent, such as hydrochloric acid or acetic acid. However, the acidity of the solution prevents the CO_2 absorption reaction, and the pH of the solution should be changed by removing acid or addition of base. This operation makes the process cost expensive. A process that enhances the carbonation reaction by changing the reaction pressure has also been proposed [10], as has swinging the pH of the reaction fluid by adding acid for the extraction reaction, and after that, adding base for CO_2 absorption [12]. However, these processes have disadvantages in that they consume large amounts of energy during CO_2 compression or the impossibility of re-using the reaction solution. The authors have developed a new CO_2 mineral sequestration process [13] that proceeds under mild conditions (under 80 °C, atmospheric pressure) and enables recycling of the reaction solution. The reaction utilizes wastes such as steelmaking slag or waste concrete as the alkaline-earth metal source.

In this paper, the feasibility of the proposed process for the industrial CO_2 sequestration process is discussed. First, the reaction mechanisms are discussed and a theoretical conversion is calculated from Gibbs free energy. Second, the reactions are experimentally assessed. Third, the feasibility of the process on an industrial scale is discussed from the viewpoint of power consumption.

2. Design of a new CO_2 mineralization process

A pH swing reaction for the CO_2 mineralization process has been reported by Park and Fan [12]. The reaction has an advantage in that the mineral extraction reaction and the carbonation reaction could be carried out under appropriate pH conditions; i.e., acidic conditions for extraction and basic conditions for carbonation. However, adding acidic/basic reagents or removing acidic reagents by heating the solution is required in order to change the pH of the solution.

We propose a new process with a recyclable reaction solution, which is capable of swinging the pH of the solution spontaneously by extracting the alkaline-earth metal and precipitating the carbonate. The details of these reactions are described below.

The process proposed in this paper consists of the following two steps (existing calcium is estimated from the amount of $2CaO \cdot SiO_2$ in the calcium source):

$$4NH_4Cl(a) + 2CaO \cdot SiO_2(s) \rightarrow 2CaCl_2(a) + SiO_2(s) \downarrow + 4NH_3(a) + 2H_2O(l) \text{...Ca extraction step.} \quad (1)$$

The calcium ion is extracted from calcium silicate by reacting with ammonium chloride solution. The acidity of the ammonium chloride solution enhances the extraction reaction of the calcium ion. The solution shows alkalinity as the reaction proceeds because of the generation of ammonia. The solubility of NH_3 in water under 1 atm was calculated as 14.0 (at 40 °C) −1.9 (at 90 °C) (mol/L) with an Aspen Plus® (Aspen Technology, Inc.) simulator by using the Peng-Robinson property method, thus all NH_3 on the right-hand side of Eq. (1) dissolves in the NH_4Cl solution if the concentration of NH_4Cl is below 1.9 mol/L. In the extractor, air exists in dead space, thus the mass fraction of NH_3 in the vapor phase/total amount was calculated in the system of H_2O, NH_3 and N_2. In the extractor, the fraction of gaseous volume with respect to the total volume was estimated as 1/5 and the pressure was estimated as 1 atm. The calculation result gave: 0.19% for 90 °C and 0.05% for 40 °C. These ratios are small enough to affect the conversion of the reaction.

$$4NH_3(a) + 2CO_2(a) + 2CaCl_2(a) + 4H_2O(l) \rightarrow 2CaCO_3(s) \downarrow + 4NH_4Cl(a) \text{ ... } CO_2 \text{ absorption and } CaCO_3 \text{ precipitation step.} \quad (2)$$

When CO_2-containing gas is in contact with the extraction solution, $CaCO_3$ is generated as in Eq. (2). The alkalinity of the solution enhances the absorption of CO_2 into the solution. The NH_4Cl solution for the extraction solution in step 1 is regenerated with the precipitation of $CaCO_3$. CO_2 is recovered as $CaCO_3$ in solid form and discarded or reused industrially. Since an inert gas, such as nitrogen is contained in the practical effluent gas compositions, NH_3 and H_2O will escape into the flue gas, a cooling tube cooled with ice water was required to be connected during the experiments of the extraction reaction. Therefore, a NH_3 recovery tower was added to the process downstream of the gas flow from the CO_2 absorption tower for the process flow diagram.

Fig. 1 shows the reaction steps and changes in Gibbs free energy and enthalpy of each reaction of (1) and (2) at the temperature of 80 °C. The Gibbs free energy and enthalpy were calculated using computer software (HSC Chemistry Version 5, Outokumpu Research Oy, Finland). The changes in Gibbs free energy and enthalpy are −9.0 and −35.1 kJ for reaction (1), and −124.5 and −161.6 kJ for reaction (2), respectively. The thermodynamic conversion calculated from ΔG was 72% for reaction (1) and 100% for reaction (2) at 80 °C. Calculation of the change in enthalpy

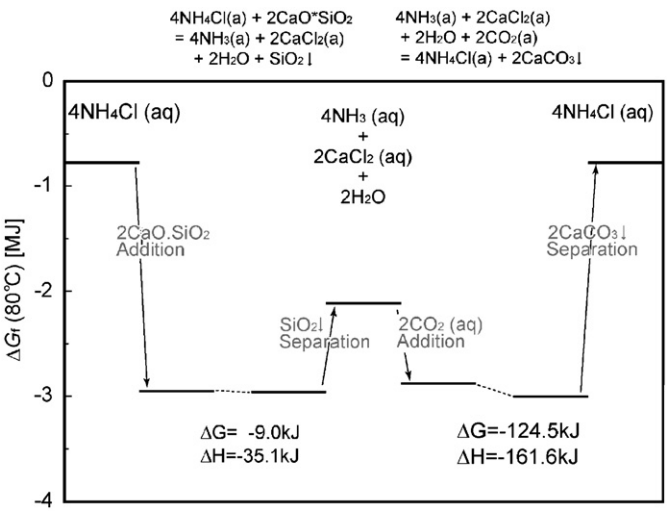

Fig. 1. Flow of reaction and changes in enthalpy.

showed that the reactions were exothermic, and as such, this process could be applicable to an energy saving CO_2 fixation process.

The advantages of the proposed process can be summarized as follows:

1. CO_2 is converted to solid $CaCO_3$, a chemically stable and non-toxic material.
2. Separation and fixation of CO_2 are carried out simultaneously in a single process.
3. Reuse and reduction of waste materials are possible. (A new treatment method for the waste materials.)
4. The energy consumption involved in the CO_2 separation and regeneration of the reaction solution is small. (There is no need to heat the CO_2 absorption solution which is required in the regeneration of general absorption methods.)

3. Experimental

3.1. Materials

In this study, converter slag was used as a calcium source, of which the particle size was smaller than 20 mm. The slag was crushed and ground using a 1.6 L of stainless steel pot-mill charged with 200 g of sample and 2 kg of stainless steel balls (25 mm in diameter). After crushing, the sample was sieved into the ranges of <63, 63–125, 125–250, 250–500, 500–1000 and 1000–2000 μm. The particle size distribution of the crushed sample is shown in Fig. 2. The particle size distribution was well correlated with the Rosin–Rammler distribution, and 80% passing size of the slag sample was calculated as 440 μm. This was used in the estimation of crushing energy (4.4). The ground samples were calcined at 950 °C for 30 min before experimental reactions in order to remove CO_2 and H_2O, which were adsorbed after production of the slag. After mixing

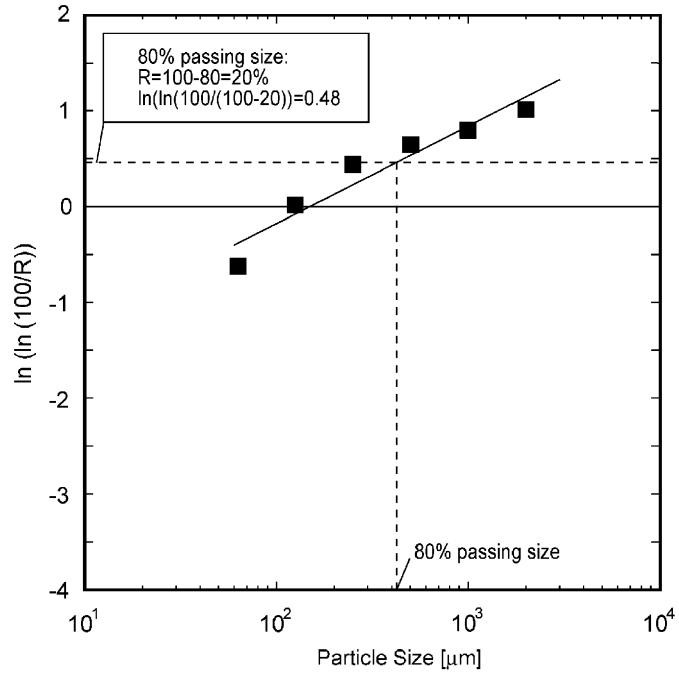

Fig. 2. Particle size distribution of a crushed slag sample (plotted on Rosin–Rammler plot). *R*, mass % of slag on the sieve; ■, percentage of material larger than the mesh size; solid line, Rosin–Rammler distribution.

with a v-shaped mixer, the samples were stored in sealed bottles until required for the experiments to prevent the occurrence of experimental errors led from inhomogeneous moisture and CO_2 absorption to the sample. The extraction experiments were carried out with every sieved and calcined sample. The specific surface areas of the slag samples were analyzed with a Micromeritics ASAP-2020 analyzer. The chemical composition of the steelmaking slag used in this study was analyzed as following; CaO: 44.5%, Fe_2O_3: 19.1%, MnO: 2.1%, Al_2O_3: 2.3%, MgO: 7.6%, SiO_2: 9.28%, P_2O_5: 1.3% (weight % in oxidation, average of <125 μm sample). The compositions were approximately the same, independent of the sizes of the particles. However, the calcium content became smaller as the particle sizes increased (43.1 wt% in the 2000 μm sample).

3.2. Extraction of calcium from steelmaking slag

Calcium extraction experiments from steelmaking slag were performed as follows; 40 ml of ammonium chloride aqueous solution (1.0 N, prepared from high grade reagent, manufactured by Wako Specialty Chemicals) was poured into a 100 ml flask placed in a water bath and heated. After reaching the experimental temperature, a steelmaking slag sample was placed into the flask. The slag sample was weighed to establish the stoichiometric amount of calcium. For example, the content of NH_4Cl in 40 ml solution was 0.04 mol, and 2 mol NH_4Cl reacts with 1 mol of CaO (MW = 56). The 63–125 μm slag sample contained 44.5 wt% of calcium (as CaO), thus the required amount

of slag (w_{slag}) was calculated as follows:

$$w_{slag} = \frac{(0.04\ (\mathrm{mol})/2) \times 56\ (\mathrm{g/mol})}{(44.5\ (\%)/100)} = 2.517\ (\mathrm{g}). \quad (3)$$

The slurry was stirred with a magnetic stirrer at a rate of 300 rpm for 1 h. The rotation speed was monitored using a tachometer (ONO SOKKI, HT-4100). After 1 h, the solution was immediately filtered through a PTFE membrane filter (Millipore, 0.2 μm pore size and 47 mm diameter). After the pH measurement (Mettler Toledo, MP 125), the filtrate was diluted 800-fold and analyzed with an ICP-ES (Shimadzu Corporation, ICPS-5000 ver. 2) analyzer for concentrations of Ca, Mg, Al, Fe and Mn. Extraction from the slag using HCl and CH_3COOH as an acid solution was also carried out in the same way. The conversion of the alkaline-earth metal for the extraction reaction x_e (%) is expressed as

$$x_e = \frac{W_{Ca\text{-}ex}}{W_{Ca\text{-}total}} \times 100, \quad (4)$$

where $W_{Ca\text{-}ex}$ is the amount of calcium in the extraction solution (g) and $W_{Ca\text{-}total}$ is the total amount of calcium contained in the slag sample used for the reaction (g). $W_{Ca\text{-}total}$ is expressed as

$$W_{Ca\text{-}total} = W_{slag} \times \frac{C_{Ca\text{-}slag}}{100}, \quad (5)$$

where W_{slag} is the weight of slag used for the extraction reaction (g) and $C_{Ca\text{-}slag}$ is the calcium content in the slag (wt%). $W_{Ca\text{-}ex}$ in Eq. (4) is expressed as

$$W_{Ca\text{-}ex} = \frac{C_{Ca\text{-}ICP\text{-}ex}}{1000} \times 800 \times \frac{40}{1000}, \quad (6)$$

where $C_{Ca\text{-}ICP\text{-}ex}$ is the concentration of calcium ions in the diluted extraction solution, obtained by ICP analysis (mg/l). The volume of solution was 40 ml for the extraction reaction, and the solution was diluted for ICP analysis. The experimental error for the extraction conversion is estimated to be 1.5% (two sigma), and the exact deviation in four experiments (80 °C, <63 μm samples) was 4%. The selectivity for calcium extraction S_{Ca} was defined as follows:

$$S_{Ca} = \frac{C_{Ca\text{-}ICP\text{-}ex}}{\sum C_{metals\text{-}ICP\text{-}ex}}, \quad (7)$$

where $C_{metals\text{-}ICP\text{-}ex}$ represents the concentration of each metal analyzed by ICP, i.e., Ca, Mg, Mn, Al and Fe.

After the extraction of alkaline-earth metal, the change in morphology and chemical composition of the slag particle surface was analyzed with a scanning electron microscope (SEM, Hitachi Ltd., S-5000) equipped with an energy dispersive X-ray analyzer (EDX, HORIBA Ltd., EMAX-5770). Before analysis, the sample was embedded in epoxy-resin and cut with a diamond cutter, and then the piece was coated (Hitachi Ltd., E102) with conductive carbon.

3.3. Adsorption of CO_2 and precipitation of $CaCO_3$

CO_2 adsorption and $CaCO_3$ precipitation was carried out as follows; 40 ml of the extraction solution obtained in the Ca extraction reaction from <64 μm size of slag under 80 °C was poured into a 100 ml three-neck flask and placed in a water bath. The concentration of Ca in the solution was determined to be 0.29 mol/L. A reflux cooling tube, pH electrode and gas injection tube were connected to the flask. A mixture of CO_2 (99.999%, Sumitomo Seika) and N_2 (99.99%, Ueno gas) gas (13% CO_2) was introduced into the flask at a rate of 17 sccm for 2 h. The flow rates of each gas were controlled using a mass flow meter. The reflux tube was cooled with ice water to prevent NH_3 and H_2O escaping from the flask with the unreacted gas. After the experiment, $CaCO_3$ was filtrated and caked. The filtrate was diluted 800-fold and analyzed by ICP. The conversion of the $CaCO_3$ precipitation x_p (%) is expressed as

$$x_p = \frac{C_{Ca\text{-}ex} - C_{Ca\text{-}fil}}{C_{Ca\text{-}ex}} \times 100, \quad (8)$$

where $C_{Ca\text{-}fil}$ represents the concentration of Ca in the filtrate, as analyzed by ICP (mg/l). The experimental error for this reaction was estimated to be 2.8% (two sigma).

The cake was washed with distilled water and dried in an oven at 110 °C for 6 h. The purity of the obtained $CaCO_3$ particles was analyzed by inductively coupled plasma emission spectroscopy (ICP-ES) by dissolving in HCl solution. The obtained particles were analyzed by X-ray diffraction (XRD, Rigaku Corporation, RINT 2000) and SEM. Before SEM analysis, the sample was coated with Pt–Pd alloy.

4. Results and discussion

4.1. Capacity of the CO_2 sequestration process

In this study, the calcium component in the steelmaking slag was selected as an alkaline-earth metal source. In Japan, the production of steelmaking slag (summation of Blast Furnace Slag and Steel Slag) is estimated to be approximately 39 million tons per year in 2005 [14]. Steelmaking slag typically contains 25–55 wt% of calcium (as CaO). Assuming the slag contains 40 wt% calcium, the amount of calcium emission is calculated to be approximately 16 million tons. Since 1 mol of CaO (molecular weight = 56) reacts with 1 mol of CO_2 (molecular weight = 44), thus the maximum potential for CO_2 storage is calculated to be 12 million tons, which is 1% of the total annual CO_2 emission (1.29 billion tons in 2005) in Japan. Although all of the steelmaking slag is not available for CO_2 sequestration, if half of the total emission could be used for this method, the potential for fixing becomes several million tons of CO_2. Calcium silicate is also contained in waste concrete and natural ore (such as wollastonite), therefore, this process is expected to have great potential as a CO_2 sequestration process.

4.2. Extraction of calcium

First, the change in the conversion of extraction reaction versus reaction time was observed. Fig. 3 shows that the concentration of calcium in the extraction solution of a small sample (<63 μm) stabilized after several minutes, while that of a larger sample (1000–2000 μm) slowly increased. For both cases, the concentration stabilized within 60 min. Therefore, the reaction time for the following experiments was set as 60 min in order to ensure that the extraction reaction stabilized for all ranges of the experimental conditions. As shown in Figs. 2 and 3, the thermodynamic equilibrium conversion for the extraction reaction was 72% at 80 °C. The conversion was higher than the experimentally obtained conversion, because of the insufficient contact of liquid with solid which existed inside of the particle.

The selectivity of the calcium extraction was 99% (Table 1). In order to explain the reason for the high selectivity of calcium ion extraction, comparisons of the selectivity of the metal ions between the extraction solution of the slag with HCl, CH_3COOH and NH_4Cl solution, were carried out. As mentioned in Table 1, only the NH_4Cl solution extracts Ca in very high selectivity. This is because the pH of the NH_4Cl solution after extraction (9.41) is in a range that only Ca could extract (8.0–10.5), while the pH values of the HCl solution (3.72) or CH_3COOH solution (5.32) are in a range that can extract magnesium (pH < 7.5) or manganese (pH < 7.0). The pH values for Ca, Mg and Mn dissolution were calculated using a chemical reaction simulator (Stream Analyzer 2.0, OLI systems, Inc.). The metal ions were estimated to exist as hydroxide ions as the initial condition, because of the limitation of the library of the program.

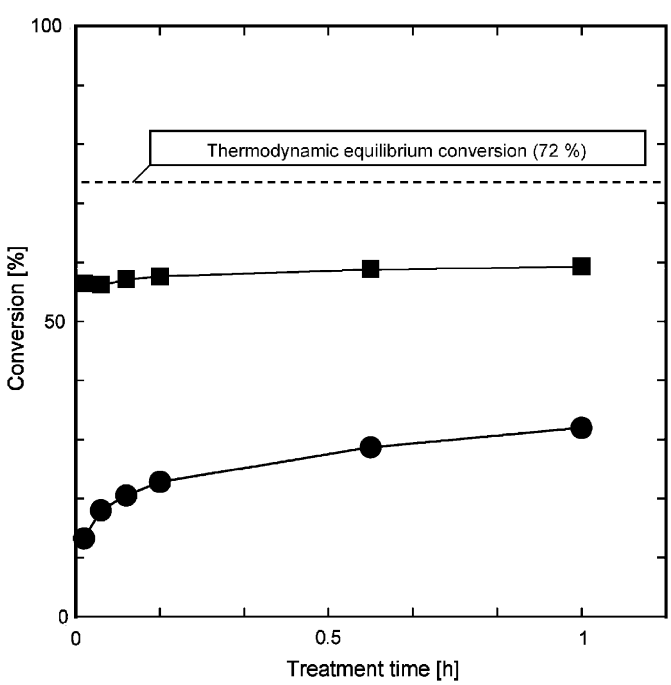

Fig. 3. Changes in the conversion of extraction reaction versus treatment time. ■, conversion (<63 μm particle size); ●, conversion (1000–2000 μm particle size).

Table 1
Compositions, pH values, and conversions of the calcium extraction reaction for various solutions

	HCl	CH_3COOH	NH_4Cl
Concentrations in extraction solution (ppm)			
Mg	1.50	2.29	0.05
Al	0.45	0.48	0.00
Ca	22.69	20.38	14.85
Mn	0.52	0.01	0.00
Fe	0.01	0.01	0.00
pH before extraction	0.12	2.37	4.63
pH after extraction	3.72	5.32	9.41
pH after precipitation	3.41	3.34	7.26
Selectivity of Ca	90.2	88.0	99.6
Ca extraction (%)	91.0	81.7	59.5

Extraction reagent: HCl, CH_3COOH, and NH_4Cl.

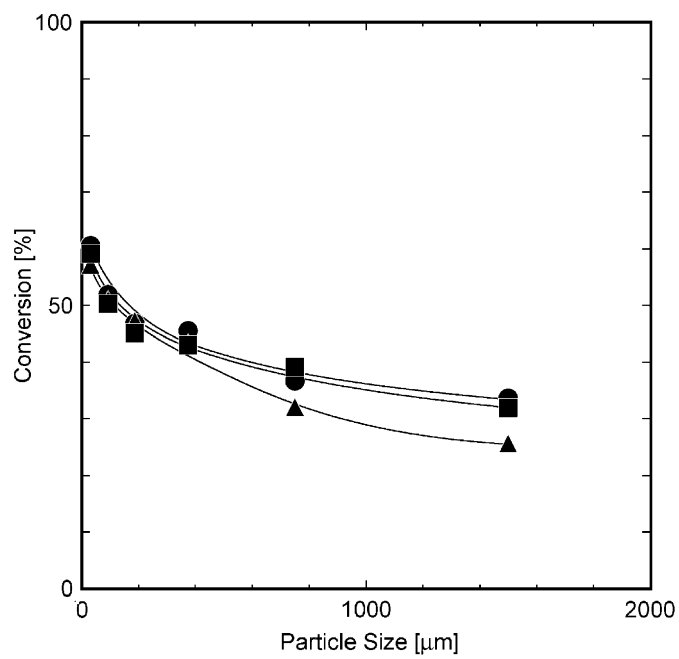

Fig. 4. Effects of the particle size of the steelmaking slag on the conversion of extraction reaction. Reaction time: 1 h; extraction agent: 1.0 N NH_4Cl. Reaction temperature: ●, 90 °C; ■, 80 °C; ▲, 40 °C.

The conversion of the extraction reaction is strongly influenced by the particle size of the alkaline-earth metal source [2,8,10,12], thus, extraction reactions were carried out for different particle sizes of the slag. The conversion of the extraction reaction for each size of particle is shown in Fig. 4. The conversion improved as the particle size became smaller, with the maximum conversion found to be 60%. The influence of reaction temperature on the conversion of the extraction reaction is also shown in Fig. 4. It was confirmed that the extraction reaction was accelerated by high temperature condition. Especially, the difference in conversion is noticeable in larger sized particles, where the

temperature was between 60 and 80 °C. However, the effect was not significant compared with the effect of the particle size. The relationship between the surface area of the slag existing in a unit volume of reaction solution and the conversion is plotted in Fig. 5. If the conversion is controlled only by the reactive surface area, then the plot should be on a straight line. However, the conversion reached a limitation around 50–60%, thus, some limitation for conversion may exist. One possible reason for the limitation is that the deposition of an inert layer, such as SiO_2, on the reactive surface limited the diffusion of the extraction solution into the particles. Other research groups reported that an inert layer deposited on the surface of the particles during extraction inhibited the contact of the particle surface with the reaction solution [12]. In order to confirm the generation of such a layer, the cross-section of the extraction residue was observed with SEM-EDX (Fig. 6). Silicon exists on the surface of the particles in high concentration compared with the bulk of the particles. This layer is supposed to inhibit the contact with the calcium resulting in a degradation of the conversion.

4.3. Absorption of CO_2 and precipitation of $CaCO_3$

The solution obtained in the calcium extraction process reacted with CO_2 in the absorption process (Eq. (2)) and produced $CaCO_3$. The extraction solution of HCl or CH_3COOH (the composition is described in Table 1) did not generate calcium carbonate by contact with CO_2, because $CaCO_3$ dissolves under acidic condition (i.e. pH < 5.7). Although the theoretical conversion should be

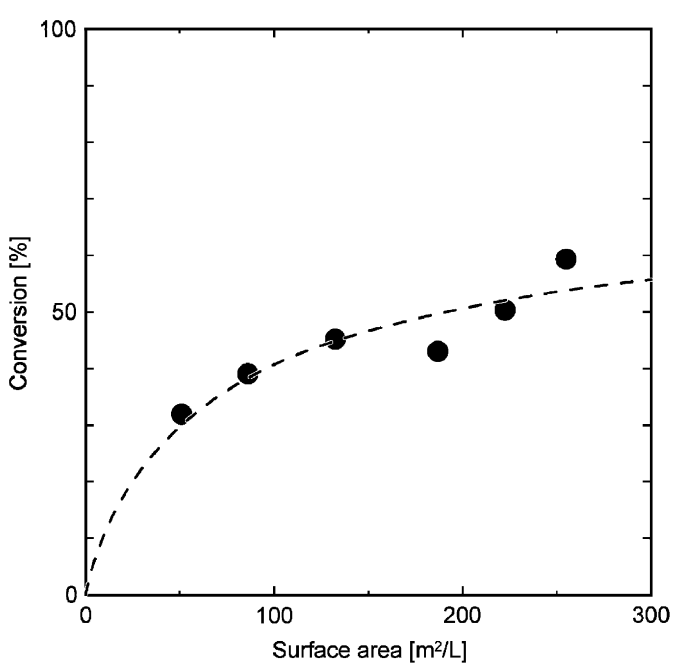

Fig. 5. The relationship between the surface area of the slag existing in a unit volume of reaction solution and conversion.

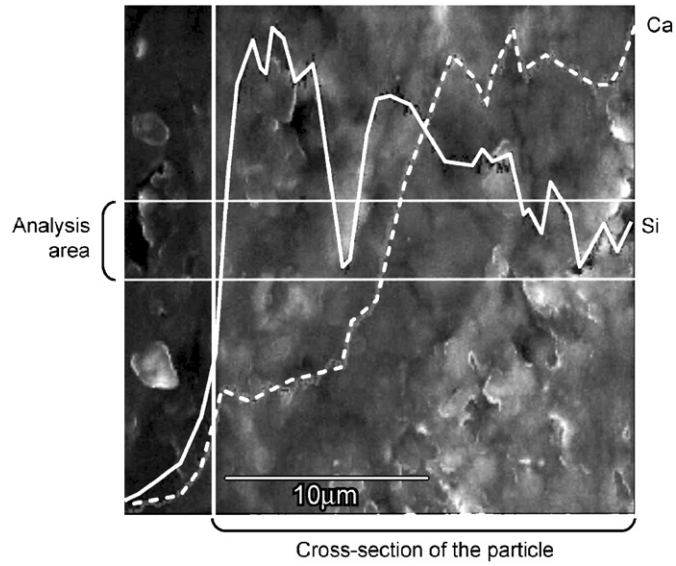

Fig. 6. Variation of Si and Ca concentration in a cross-section of the extraction residue (1000 μm). Solid line: concentration of Si; dotted line: concentration of Ca.

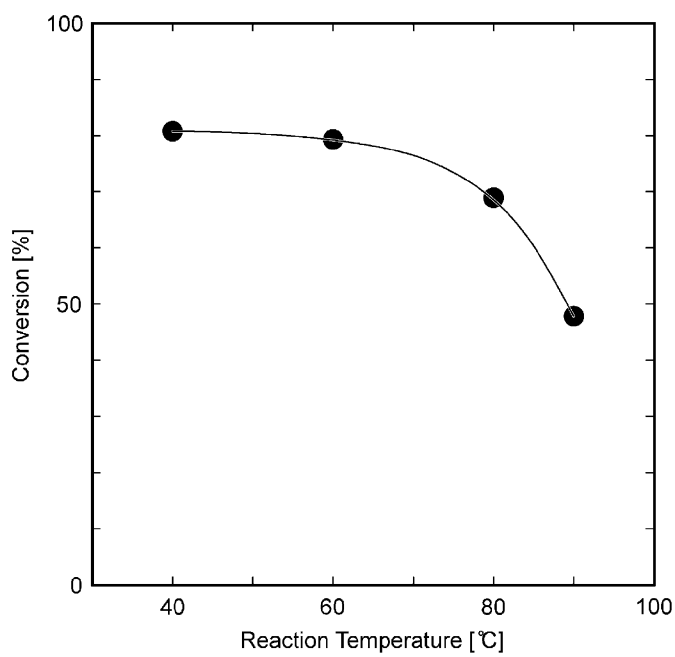

Fig. 7. The relationship between the conversion of precipitation reaction and reaction temperature. Reaction time: 1 h; solution: extraction solution from <63 μm slag; reaction temperature = 80 °C.

100% from a thermodynamic calculation, it was supposed that the reaction temperature is supposed to influence the solubility of CO_2. Therefore, the effect of the reaction temperature on the conversion of the precipitation reaction was analyzed to define the appropriate conditions for precipitation. The conversion was calculated from the concentration of calcium ions, as shown in Eq. (6). The relationship between the conversion and reaction temperature is shown in Fig. 7. From this figure, it is confirmed that the absorption of CO_2 was enhanced under a

low-temperature condition. The reason for this was expected to be due to inadequate contact between the gas and liquid, and the solubility of CO_2 with temperature. For the process design, a reaction temperature higher than 80 °C is unfavorable, although the conversion for the extraction reaction is high at higher temperatures.

$CaCO_3$ obtained from this process is expected to be commercially useful as paper filler if the chemical properties of the obtained particles meet the requirement for practical applications. Therefore, the $CaCO_3$ particles obtained in the precipitation step were analyzed with SEM and XRD in order to clarify the effect of the reaction temperature on the morphology of the particle. The SEM photographs of the $CaCO_3$ samples for each reaction temperature are shown in Fig. 8. It was found that the cubic particles (calcite) in the samples were formed at lower temperatures ((a) and (b) in the figure). As the reaction temperature became higher, the fraction of calcite decreased and plate-shaped ((c) in the figure) or needle-shaped ((d) in the figure) particles were observed. The XRD patterns of these samples showed that aragonite was generated in high reaction temperatures (Fig. 9). The results showed that the morphology of the $CaCO_3$ particles is controllable under the range of this experimental condition, and this will help the utilization of $CaCO_3$ in industrial applications. The purity of $CaCO_3$ was measured and found to be up to 98%; thus the possibility of obtaining pure $CaCO_3$ by this process was confirmed from this result.

4.4. Estimation of energy consumption

Energy consumption of the proposed process was evaluated based on the assumption that this process was applied to the treatment of 100,000 Nm^3/h of flue gas

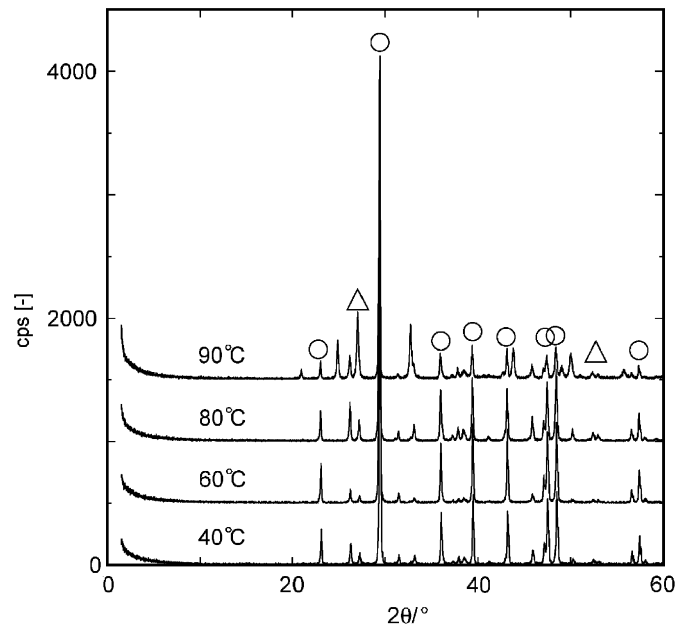

Fig. 9. XRD patterns of $CaCO_3$ samples for each reaction temperature. ○, calcite; ρ, aragonite.

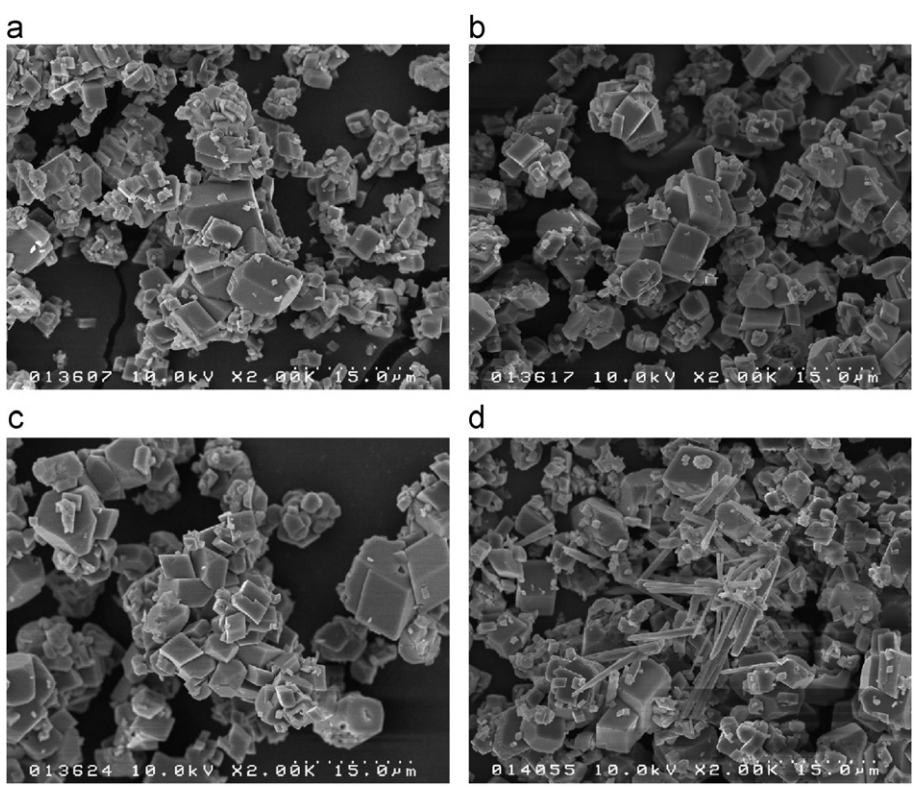

Fig. 8. SEM photographs of $CaCO_3$ samples for each reaction temperature: (a) 40 °C, (b) 60 °C, (c) 80 °C, and (d) 90 °C.

(13% of CO_2, 87% of N_2). The reaction temperature for extraction and precipitation was decided to be 80 °C from the experimental analysis. The degree of Ca extraction from slag was determined to be 48.1%, which was calculated from the particle size distribution of the crushed sample (Fig. 2) and the conversion of the extraction reaction (Fig. 4). It was estimated from the material balance that the absorbed CO_2 was 22.9 t/h, the required slag was 141.4 t/h, the generation of $CaCO_3$ was 52.3 t/h, and the extraction residue was 112.0/h (Fig. 10). The calculation basis of the power consumption was listed in Table 2. The estimation of the power consumption of each piece of equipment was conducted as follows:

The power consumptions for the Absorber and pumps were estimated from the existing plant capacity, estimating the scale factor = 0.7.

The power consumption in the crushing process was estimated using Bond's equation:

$$W = W_i\left(\frac{10}{\sqrt{W_{P80}}} - \frac{10}{\sqrt{W_{F80}}}\right), \tag{9}$$

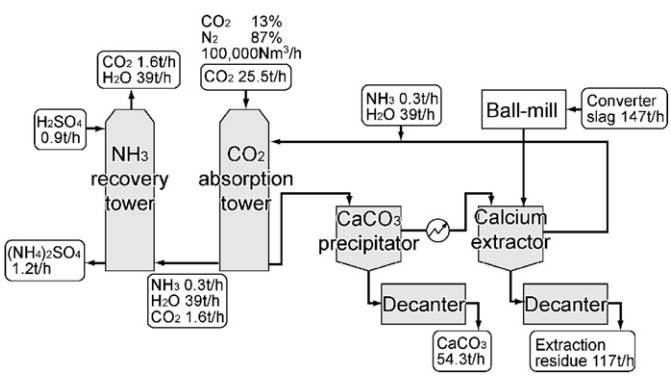

Fig. 10. Block flow and material balance of this process.

where W is the power consumption (kWh/t), W_i is the work index of the slag (30.4 kWh/t-slag obtained from the ball—mill crushing test of the slag sample), W_{P80} refers to the size (80%) of crushed sample passed, as shown in Fig. 2 (440 μm), and W_{F80} refers to the size (80%) of the feed sample passed (20,000 μm).

The power consumptions for solid–liquid separation were estimated from the capacity and power consumption of existing equipment. The total power consumption was calculated by multiplying the power consumption of each unit equipment to the round out value of throughput/capacity.

The heat duty for the solution was calculated as follows: the solution was cooled because of the evaporation of water in the CO_2 absorption tower, while it was heated by reaction heat during calcium extraction. The material and heat balance in the absorption tower were calculated using a Stream Analyzer. The result showed that the solution was cooled from 80 to 74 °C and required 8400 kWh of energy for heating the solution to 80 °C. On the other hand, the reaction heat of the extraction was 2650 kWh. Thus, the heat duty required to maintain the temperature of the reaction solution became 5750 kWh. The power consumption for heating (2300 kWh) listed in Table 2 was calculated by multiplying the heat duty (5750 kWh) by 0.4, which is the net efficiency of an electric power plant.

Taking into account these values, the total energy consumption in this process is roughly estimated to be 300 kWh/t-CO_2, which is smaller than other CO_2 sequestration processes (470–640 kWh/t-CO_2 for amine absorption and geological sequestration [15]) and this process is favorable from the viewpoint of power consumption. More than half of the process power consumption came from the slag grinding process, and the grinder requires high construction costs. Furthermore, the emission of NH_3 downstream of the CO_2 absorber must be removed,

Table 2
The calculation basis of material flow and power consumption

Process	Equipment	Amount to be treated	Power consumption per unit equipment (kWh)	Capacity	Power consumption (kWh)
Adsorption	Absorber (blower)[a]	100,000 Nm^3/h	250	100,000 Nm^3/h	250
Extraction	Crusher (ball mill)[b]	147.0 t/h	12.4	1 t/h	1820
	Solid–liquid separator (decanter)[c]	248.9 t/h	76	14 t/h	1370
Precipitation	Solid–liquid separator (decanter)[c]	116.2 t/h	76	14 t/h	680
Pump etc.	Motor[a]	1210 t/h	646	964 t/h	760
Heating	Steam[d]				2300
Total					7180 (300 kWh/t CO_2)

[a]Estimated from existing plant capacity and power consumption.
[b]Estimated from Bond's equation.
[c]Estimated from existing equipment.
[d]Calculated from energy balance of reactions.

because 1.5 t/h of the NH_3 evaporates in the CO_2 absorber. Therefore, the development of weak base reagents having lower vapor pressure should be carried out.

5. Conclusion

A new CO_2 mineral sequestration process that utilizes the pH swing of an ammonium chloride solution was proposed. A thermodynamic analysis of the calcium extraction reaction obtained from a calcium silicate ($2CaO \cdot SiO_2$), CO_2 adsorption reaction and $CaCO_3$ precipitation reaction showed that each reaction proceeded spontaneously and the total process was exothermic. The experimental analysis was also carried out using steelmaking slag as the calcium source. The experimental results showed that the conversion of the calcium extraction reaction reached 60% with high selectivity. Pure $CaCO_3$ generation was also confirmed. The energy consumption of this process was roughly estimated as 300 kWh/t-CO_2. These results showed that this process is a prospective one from the viewpoint of low power consumption compared with the previously reported processes, though it has problems related to the high cost of crushing slag and the recovery and supply of NH_3.

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