Development of a new carbon dioxide sequestration scenario by the carbonation of waste cement

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Introduction

Sequestrations of CO_2 in the form of carbonates of calcium or magnesium could realize more environmentally benign scenarios because these compounds are extremely stable in the environment. For the implementation of the CO_2 sequestration scenarios in the form of the carbonates, however, a tremendous amount of calcium or magnesium sources is required for the handling of continuous effluent of anthropogenic CO_2. Natural rocks containing calcium or magnesium such as serpentinite [1] or wollastonite [2] have been tested as alkaline earth metal sources for carbonate formation. Although thermodynamic calculations indicate that carbonate formation reactions can proceed spontaneously, the observed reaction rates are extremely slow when these sources were reacted with CO_2 under rather mild conditions. Thus, an appropriate acceleration method is needed for the practical use of the carbonate formation for practical CO_2 sequestration. Several acceleration methods have been examined so far including; increasing of the surface area of rock particles by pulverization [3], use of acceleration medium such as hydrochloric acid [4] or acetic acid [2], and application of high temperature and pressure conditions, where CO_2 is in the supercritical state [1]. Although considerable acceleration of the reaction rates were realized by these methods, they may require more energy consumptions, or treatment of waste acids. In this paper, we proposed a new scenario of CO_2 sequestration by using waste cement as a calcium source for the carbonate formation. Waste cement is a calcium-rich waste product containing calcium in the form of calcium silicate hydrate (such as C_3S; $3CaO \cdot 2SiO_2 \cdot 3H_2O$) and calcium hydroxide ($Ca(OH)_2$). Thus, waste cement is considered as a potential candidate as a calcium source for carbonate formation for CO_2 sequestration in terms of the capacity of CO_2 sequestration.

In this paper, the carbonate formation rates from a sample of waste cement were determined by laboratory-scale experiments. Based on the results, a model process was designed for the treatment of CO_2 emitted from a 100-MW thermal power plant, and evaluated the feasibility of the proposed process in terms of energy consumption and cost.

Outline of the proposed process

Outline of the proposed process is schematically illustrated in **Figure 1**. Waste concrete discharged from dismantled buildings is first pulverized, and classified into aggregates and waste cement particles. The waste cement particles are fed to a high-pressure reactor vessel for extraction of calcium ions with pressurized CO_2 and water. The CO_2 is captured and separated from a point concentrated emission sources such as a thermal power plant. In the extraction vessel, the extraction reactions of calcium ions from waste cement would take place with stirring. Due to the large solubility of $CaCO_3$ under high-pressure conditions of CO_2, extraction reaction

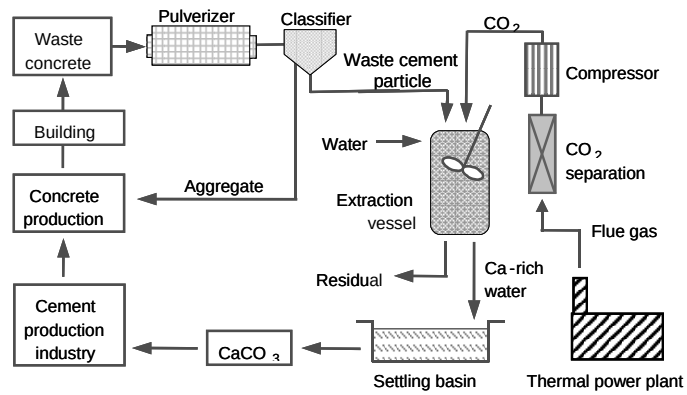

Figure 1 Schematic drawing for the CO_2 sequestration process.

will proceed in the extraction vessel. After a certain period of the extraction, the slurry is filtered and the solution phase is separated. Then, the solution was left under the atmospheric pressure in the settling bath to allow the precipitation of $CaCO_3$. The product $CaCO_3$ can be either used as a raw material of cement production industry or disposed of in appropriate sites. In the former case, the proposed process could be regarded as a recycling process of waste concrete, while the latter case as a sequestration process of CO_2.

Experimental

Waste cement particles. The waste cement sample was kindly supplied by Tateishi construction corp. as a byproduct in a practical recycling plant of waste concrete. The diameter of the waste cement particles distributed in the range of 10 – 200 μm, with a peak at about 25 - 40 μm (area based), or about 80 μm (volume based). The weight fraction of calcium was determined to be 27.3 % of waste cement.

Laboratory equipments and methods. Laboratory equipments are illustrated in **Figure 2**. A given amount of waste cement particles were dispersed in 350 mL water in the batch-type stirring vessel with 500 mL inner volume. The extraction vessel was immersed to the water bath, and heated to an extraction temperature. Gaseous CO_2 was fed to the vessel from CO_2 cylinder. A backpressure-controlling valve installed at the downstream side of the extraction reactor controlled the CO_2 pressure in the vessel. The stirring of the slurry contents in the vessel was conducted by a two-wing puddle type fin of which the stirring rate can be altered in the range of 0 ~ 1000 rpm. During the extraction experiments, the content in the vessel was sampled at a given intervals through a sintered-metal filter with 5 μm meshes. The filtered solution was then depressurized to the atmospheric pressure, and the concentration of calcium ions was determined by an inductively coupled plasma – atomic emission

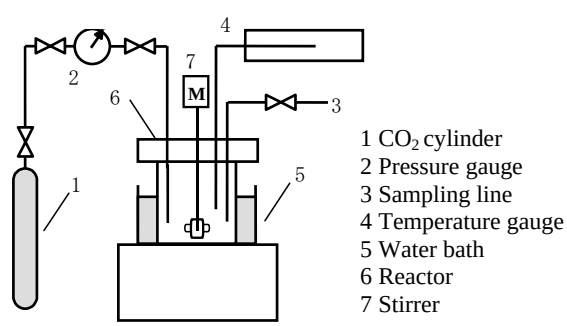

Figure 2 Schematic drawing of the experimental apparatus for calcium extraction from waste cement particles.

spectrometric (ICP-AES, Hitachi, P- 4010) method. The extraction ratio and the rate could be determined from the time course of the concentration change of calcium ions in the sampled solution.

Results and Discussion

Figure 3 shows the one typical example of time course of the calcium concentration in the sampled solution filtered from the reactor for various initial amounts of the waste concrete. For all the runs, the initial amount of water was fixed at 350 g, so that the initial weight ratio of waste cement to water was changed in the range of 0.29 wt% to 2.9 wt%. Other experimental conditions were fixed for all the runs: stirring rate = 900 rpm, temperature = 323 K, p_{CO2} = 3.0 MPa. The calcium concentration increased almost linearly with an increase in the reaction time up to about 10 min for all the cases. After that, the concentration leveled off or slightly decreased. The initial increasing rate of calcium concentration increased with an increase in the initial amount of waste cement. The sampled solution was supersaturated with calcium ions even at the early stage of the extraction reaction except the case with the smallest ratio of the waste cement/water (0.29 wt%). The extraction ratio of calcium after 3 min extraction was about 36 % for the run of the smallest ratio of the waste cement /water (0.29 wt%), and 18 % for the run of the largest ratio (2.9 wt%).

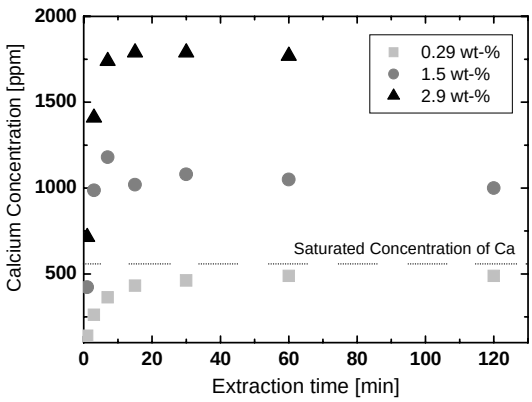

Figure 3 Change of concentration of calcium ion for various initial amounts of waste cement particles. Temperature = 323 K, stirring rate = 900 rpm, and p_{CO2} = 3.0 MPa. Dot line in the figure shows the saturated concentration of calcium ion for the extraction condition.

Process design and evaluation

Based on the experimental results, a CO_2 treatment process was designed and the energy consumption for the operation was estimated focusing the extraction step, and the effect of the extraction conditions such as CO_2 pressure, initial ratio of waste cement to, size of the waste cement particles on the process energy consumption were investigated.

As a model process, treatment of CO_2 emitted from a coal-fired 100 MW thermal power plant with 40 % overall efficiency was considered. The net amount of CO_2 emission from the power plant is 0.0174 t / s, or 5.49×10^5 t / year [5]. Since the weight fraction of active calcium content in the present sample waste cement is about 24.3 %, 2.26×10^6 t / year of the waste cement effluent is necessary to treat the total amount of emitted CO_2 from the power plant assuming 100 % conversion. Generally, cement is mixed with water of about 55 wt% of cement when using as concrete. Thus, 2.26×10^6 t / year of the waste cement is equivalent to 1.46×10^6 t / year of the cement (waste cement consists of water and cement). This number is just about 1.83 % of the total production amount of waste cement in Japan at 2001. An abundant amount of resources of waste cement is available for the treatment of CO_2.

It is assumed that the waste cement is supplied in a form of particles of which the mean diameter is about 5 cm from demolition of buildings, and pulverized to smaller particles to enhance the extraction efficiency. Bond's equation was applied for the estimation of energy required for pulverization. After pulverization, the waste cement particles are mixed with water in stirred tank type reactors, and the CO_2 gas captured from the flue gas of the thermal power plant will be introduced to the reactor to start the extraction reaction. The capture of CO_2 from the gas is conducted by a liquid absorption process with mono ethanol amine. To enhance the extraction efficiency, CO_2 will be pressurized from 0.1 MPa to the reaction pressure (such as 3.0 MPa). The CO_2 will be pressurized before introducing to the extraction reactor by an adiabatic compression with 90 % efficiency. The reactor volume was determined from the CO_2 emission rate and the retention time in the extraction reactor. The retention time is assumed 3.0 min. The reactor is divided into 20 identical reactors. The scheme for scaling-up of the reactor was carried out by adjusting the retention time and the power consumption for stirring per unit volume of the content with those of the extraction vessel used in the experiments. Only power consumption for the stirring was considered for the operation of the extraction reactors because waste heat from the thermal power plant is available for heating up the reactant to the extraction temperature.

After extraction, the solution phase and the remained particles of the waste cement will be separated by a gravitational principle in a settle basin. The solution phase was depressurized to the atmospheric pressure to make calcium carbonate particles deposit. Then the calcium carbonate particles will be disposed of in an appropriate site or recycled to the cement manufacturing industry. Energy requirement for these processes would be negligible compared with those in the extraction process and pre-treatment process before that.

Table 1 shows the energy and cost consumptions for carbon dioxide sequestration in the optimized extraction conditions. Based on the laboratory extraction experiments, the energy consumption for the proposed process to sequester CO_2 emitted from a 100 MW-thermal power plants was estimated to be 1540 kWh / t-C, and the cost was estimated to be about 83 USD / t-C. This value is comparable with the ones with the ocean sequestration scenarios, indicating that the proposed process for CO_2 sequestration is a feasible option.

Table 1 Energy and cost consumptions for carbon dioxide sequestration in the optimized extraction conditions.

	CO_2 Separation	Pressurization	Stirring	Pulverization	$CaCO_3$ selling	Total
Power Consumption [MW]	5.5	13.7	0.32	6.4	-	25.9
Energy Cosumption [kWh / t-C]	326	816	19	382	-	1543
Cost [USD / t-C]	29	73	2	34	-55	83

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