

Development of a Carbon Sequestration Process by the Carbonation Reaction of Waste Streams Containing Calcium or Magnesium

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Abstract

Carbon sequestration and utilization processes via carbonation reactions of materials containing alkaline earth metals such as calcium and magnesium were developed. The materials containing calcium studied in this study are wollastonite and waste concrete. Two types of treatment reactions were proposed and studied; a treatment process using acetic acid and direct carbonation with high pressure CO₂. Process design of each carbonation process was carried out based on laboratory-scale experimental results. The feasibility of each process was then examined in terms of the net CO₂ emission reduction, the power consumption, and cost for the carbon sequestration. It was demonstrated that these processes were promising as a measure for CO₂ sequestration, although the potential amount of the emission reduction may not be as large as the geological or ocean sequestration measures.

Introduction

Carbon sequestration via carbonation reaction of alkaline earth metal salts has been recognized as a promising option for emission reduction of CO₂ as a mitigation measure of global warming [1] [2]. Most preeminent advantage of the carbon sequestration via mineral carbonation would be the high stability of carbonates. As shown in Fig. 1, the Gibbs free energy of carbonates of alkaline earth metals would be much lower than CO₂ itself, indicating extremely high stability in the environment. On the other hand, there are two challenges for the implementation; availability of the source of minerals containing alkaline earth metals, and acceleration of the carbonation reaction. The carbonation of alkaline earth metal salts is a naturally-occurring process as “rock weathering”. The weathering reaction in the natural system would proceed with an extremely slow rate within the geological time-scale. As a mitigation measure for global warming, it is necessary to accelerate the reaction by some means. The sequestration process of via carbonation is, thus, recognized as an “accelerated weathering” process. On the alkaline earth metal sources, ultra-basic rocks such as serpentine or olivine could be potential materials for sequestration because of their

abundance of resources, and the carbonation reaction of these materials have been experimentally in laboratory scale [3]-[6]. However, carbonation of these rocks requires high pressure and high temperature conditions to achieve the reaction rate to make the process practical, which may increase the process cost and the power consumption. Other resources for the alkaline earth metal would be waste stream containing calcium or magnesium such as waste concrete, steel slug, sea shells, fly ash.

Our research group has been working on the CO₂ sequestration via mineral carbonation reaction for years with using waste streams, and several processes have been proposed and their feasibilities were examined based on the experimental studies by using a laboratory-scale apparatus [7]-[10]. In this paper, the carbonation processes developed by our group will be discussed with focusing on the process evaluation.

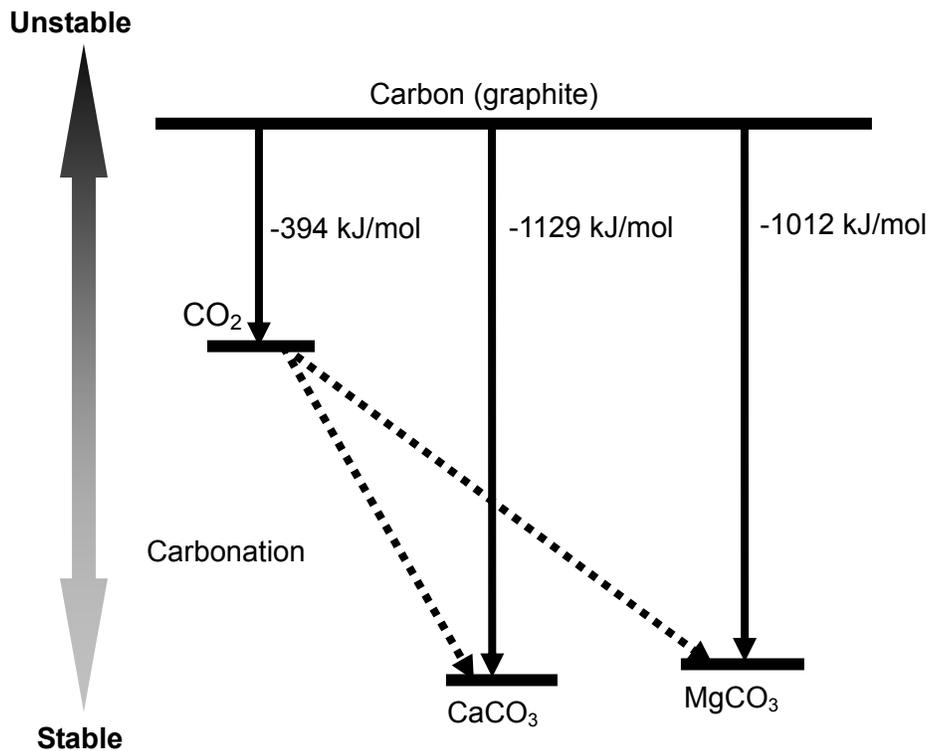


Figure 1 Gibbs free energy of compounds containing carbon atom.

Development of the mineral carbonation processes

Artificial rock weathering with acetic acid [7]

In order to accelerate the carbonation reaction, the following reaction scheme with using acetic acid as an acceleration medium for the reaction was proposed. In this process, the carbonation reaction of wollastonite (CaSiO₃) can proceed with the following two-step reaction scheme.

- Overall:



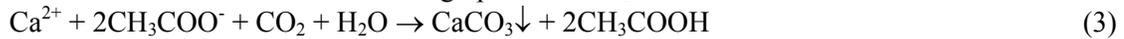
The reaction will proceed with the following two steps.

- Two-step reaction with acetic acid:

1. Extraction of calcium ions with acetic acid from wollastonite



2. Crystallization of calcium carbonate with high pressure CO_2



In the first step, particles of wollastonite will be reacted with acetic acid, and the calcium in the wollastonite will be extracted to the aqueous phase as calcium ions. After filtering the solid residue, the solution phase containing calcium ions will be reacted with high pressure CO_2 gas through bubbling (the second step). From thermodynamics, high pressure CO_2 is required to increase the deposition ratio of calcium as calcium carbonate. Acetic acid will be recovered in the second step, thus no net acetic acid will be consumed in the overall process.

The reaction rate of each steps were examined in a laboratory scale experimental apparatus under various operation conditions, and the following results were obtained.

- Extraction step

About 48% of calcium in wollastonite was extracted into the aqueous phase for 250 min at 60 °C, when the weight ratio of wollastonite, acetic acid, water was 13.26 /13.72 /50. The initial reaction rate is in proportional with the surface area of wollastonite, indicating the reaction is limited in the surface of the wollastonite particles.

- Crystallization step

About 18 % of calcium ions in the extracted solution will be deposited as calcium carbonate when CO_2 gas was reacted at 30 bar with the saturated solution of calcium acetate at 80 °C. The initial deposition rate was found to be in proportional with the square root of the CO_2 pressure.

Based on the experimental results under various conditions, process design of carbon sequestration via carbonation of wollastonite was conducted. The schematic flow diagram of the process is shown in Figure 2. The power consumption for the process was estimated assuming a CO_2 sequestration process from a 100 MW coal-fired thermal power plant. The total process power consumption was 20.38 MW, which reduces about 20 % of the efficiency of the thermal power plant. The breakdown of the power consumption was summarized in Table 1. About half of the power consumption can be attributed to the separation and compression process of CO_2 . About 1/4 of the power will be consumed for the pulverization of wollastonite. In the estimation, it was assumed the wollastonite particles with 1000 μm diameter will be pulverized to 20 μm to obtain a sufficiently high reaction rate. The total power consumption per 100-MW power generation is equivalent to 325 kWh/t- CO_2 .

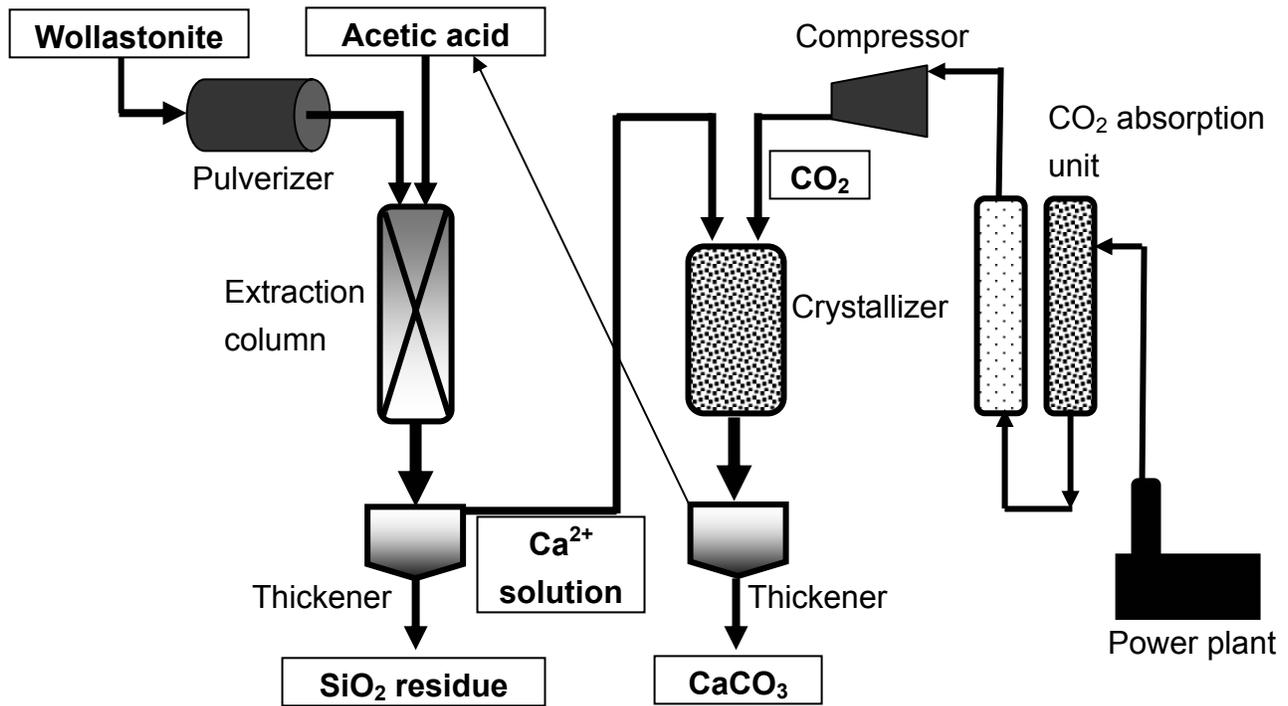


Figure 2 Schematic flow diagram for the carbonation process of wollastonite with CO₂.

Table 1 Breakdown of the CO₂ sequestration process with the carbonation of wollastonite via the two-step reaction scheme with acetic acid.

	Power consumption [MW]	Percentage
CO ₂ separation	5.56	27.28
CO ₂ compression	4.65	22.82
Pulverization	5.29	25.96
Extraction	1.27	6.23
Crystallization	2.60	12.76
CaCO ₃ separation	1.01	4.96
Total	20.38	100

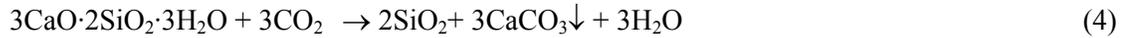
Carbonation of waste cement [8]

Concrete is a widely-used building material composed of cement and aggregates. The cement component in concrete is hydrated and combined the components including aggregates tightly. The cement component exists in the form of calcium silicate hydrate (for example, 3CaO·2SiO₂·3H₂O) and calcium hydroxide (Ca(OH)₂), and rich in calcium. Waste cement powder is generated in the process in the recycling process of aggregates from waste concrete. Due to the increasing trend in the waste concrete generation rate in Japan (37 Mt/y, containing 3.5 Mt-Ca as shown in Figure 3), calcium content in the waste cement could be utilized as a calcium source for the CO₂ carbon sequestration via carbonation reaction. The calcium components in the waste cement component seem to be more reactive than those in

calcium-containing rocks, and consequently, the carbonation reaction could proceed under milder conditions than wollastonite.

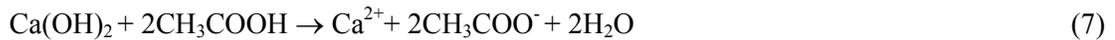
The above two-step reaction scheme was applied to waste cement powder, which was generated as a by-product of recycling process of waste concrete.

- Overall reaction:



- Two-step reaction scheme with acetic acid:

1. Extraction of calcium ions with acetic acid



2. Precipitation of calcium carbonate

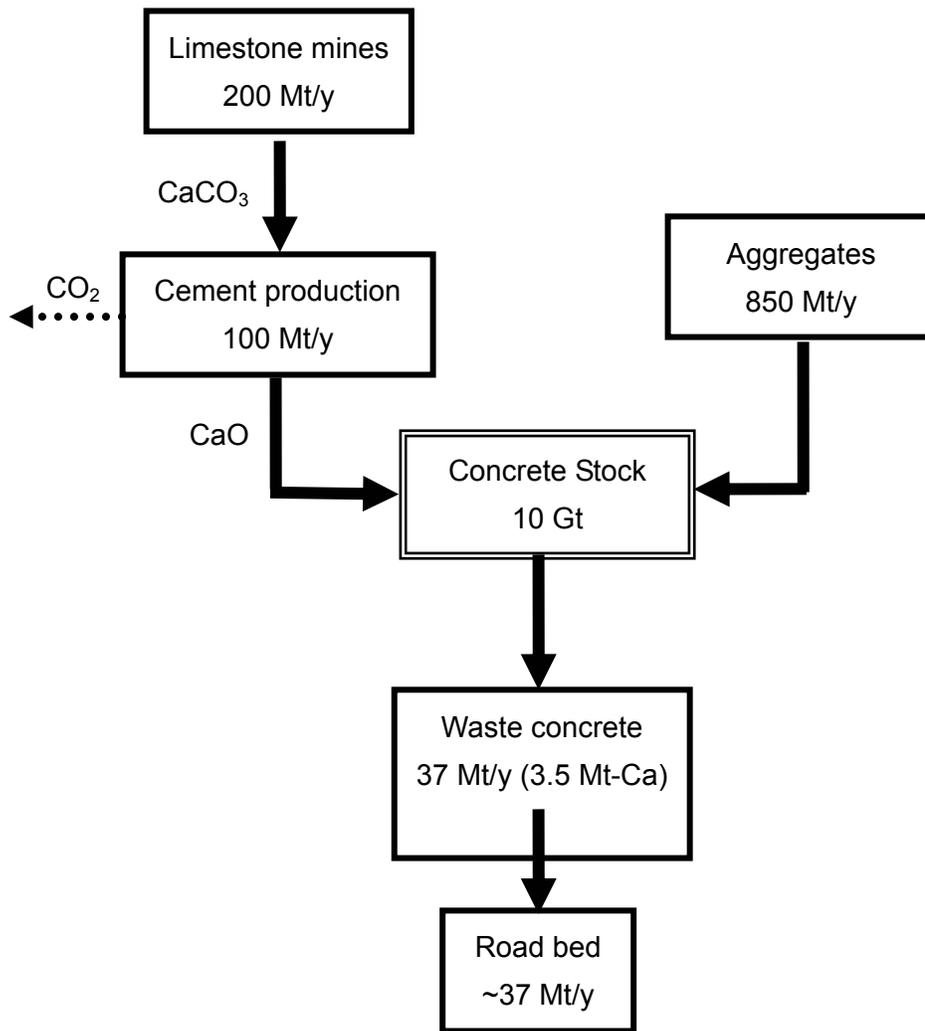


Figure 3 Material flow related to concrete in Japan.

The calcium extraction rate of the waste cement with acetic acid solution was shown in Fig. 4, with the results for wollastonite under the same condition. The average diameters of both the waste cement powder and wollastonite were 100 μm . As was expected, the extraction rate of calcium from the waste cement was much higher than that from wollastonite. Based on the experimental results, a process design for the carbonation process of the waste cement powder was conducted, and the power consumption for the process was estimated. The results are shown in Table 2. The process power consumption was reduced to about 2/3 of that with wollastonite, mainly due to the reduction of the power required for pulverization and extraction. It was assumed that the pulverization is unnecessary to obtain the waste cement powder because the cement component with 100 μm can be obtained in the recycling process of waste concrete.

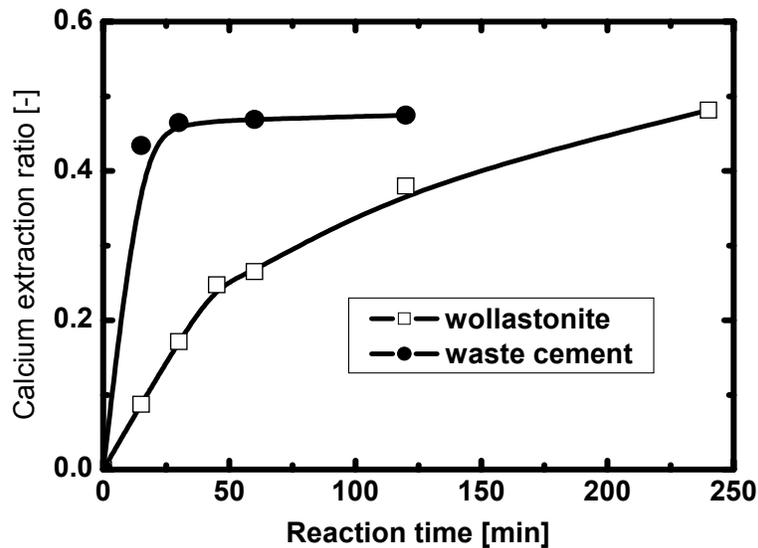


Figure 4 Calcium extraction rates for wollastonite and waste cement powder with acetic acid solution (25.76 %) at 333 K.

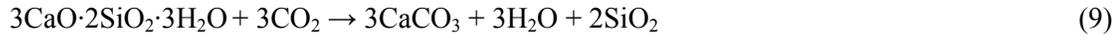
Table 2 Breakdown of the CO₂ sequestration process with the carbonation of waste cement powder via the two-step reaction scheme with acetic acid.

	Power consumption [MW]	Percentage
Pulverization	-	-
CO ₂ separation	5.56	40.0
CO ₂ compression	4.65	33.5
Extraction	0.07	0.5
Deposition	2.60	18.7
CaCO ₃ separation	1.01	7.3
Total	13.89	100

Direct carbonation process of waste cement with high-pressure CO₂ [9] [10]

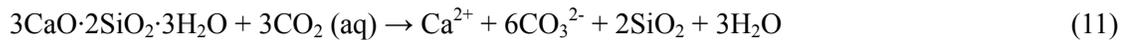
Because of the higher reaction activity of the waste cement powder, it can be anticipated that the direct reaction of the waste cement powder with CO₂ can proceed with a sufficiently high rate. Then, the following pressure-swing reaction scheme was proposed.

- Overall reaction:



- Pressure swing reaction:

1. Higher pressure CO₂ : leaching calcium ions from waste cement



2. Lower pressure CO₂ : precipitation of CaCO₃



Reactions (11) and (12) are the extraction reactions of calcium ions from waste cement with carbonic acid equilibrated with high pressure CO₂. The solubility of calcium ions in waste cement with CO₂ is an increase function of the CO₂ pressure as shown in Fig. 5. Therefore, the calcium ions will be dissolved in the aqueous phase under high pressure of CO₂; calcium ions from waste cement can be extracted with the high pressure CO₂. When the CO₂ pressure is reduced, the solubility of calcium ions will be reduced and calcium carbonate will be precipitated. The above reactions would proceed spontaneously from the thermodynamic point of view, without requiring the addition of heat to react.

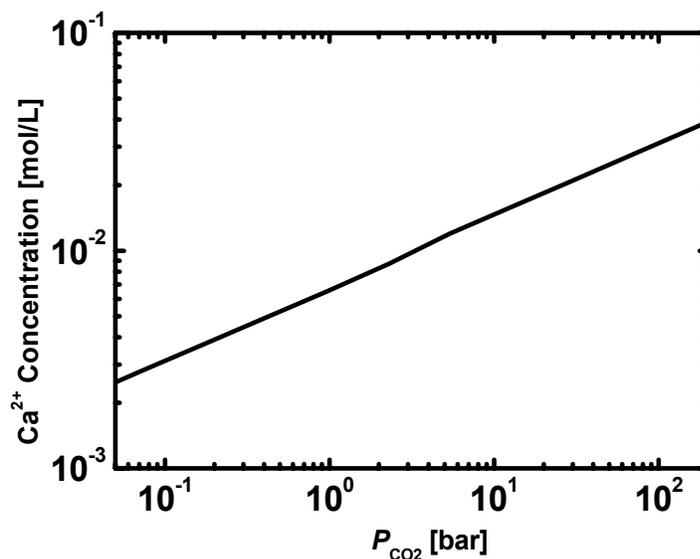


Figure 5 Solubility of calcium ions in water as a function of CO₂ in the gas phase equilibrated with the aqueous phase.

The process feasibility was examined with experimental works on the carbonation reactions under various conditions by using the same sample of waste cement powder. The results for the extraction process were shown in Figure 6. The calcium concentration in the aqueous phase could reach close to the saturation value within 20 ~30 min of the reaction time for each pressure condition. These results indicate that the extraction reaction can proceed with a reasonably high rate under high pressure conditions of CO₂. Note that when the ratio of waste cement to water in the feed is high, the calcium concentration could exceed the equilibrium solubility: supersaturation conditions can be realized.

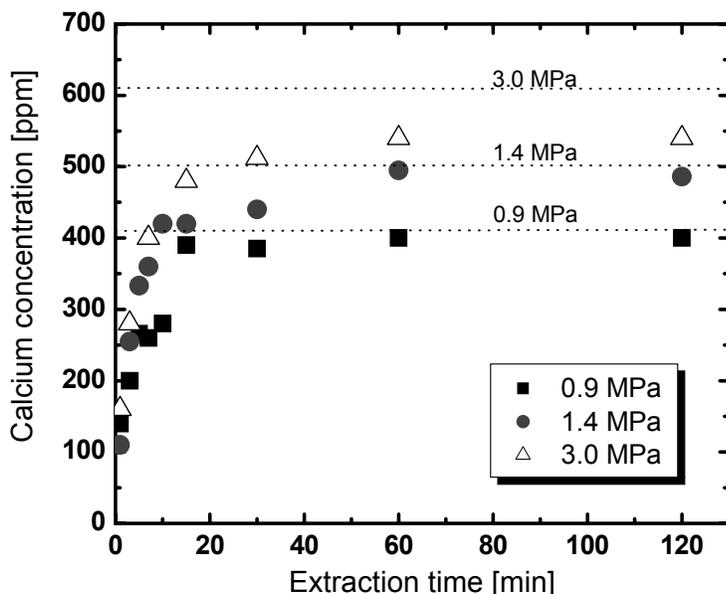
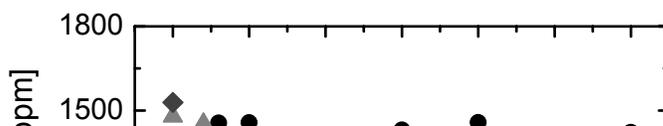


Figure 6 Effect of CO₂ pressure on the extraction reaction of calcium from the waste cement powder. Temperature = 323 K. The dotted line shows the saturated concentration of calcium under the extraction conditions used.

The precipitation processes by reducing the CO₂ pressure from the extracted solutions were experimentally studied. Figure 7 shows the calcium concentration change with the time for the precipitation reaction. The precipitation reaction may occur with a lower rate. Note that with addition of seed crystals of calcium carbonate in the extracted solution, the precipitation reaction was significantly accelerated and the purity of the product calcium carbonate was higher than 97 %, while without the addition of seed crystals, the purity of the calcium carbonate is as low as 80%.

Figure 8 shows a schematic drawing for the direct carbonation process of waste cement by the pressure swing of CO₂. Table 3 shows the estimation results for the process power consumption based on the experimental results. It is assumed that all of the CO₂ emitted from coal-fired thermal power plant will be used for the carbonation of waste cement. The power consumption per 100-MW power generation in the plant is shown in Table 3. Operating cost for the process was also shown. The process power consumption is higher than the case with acetic acid, mainly due to the pulverization of the waste cement and compression of CO₂. The pulverization of waste cement is required to increase the extraction rate. The operation cost for the CO₂ sequestration would be about USD 20, considering the revenue by selling high-purity CaCO₃.



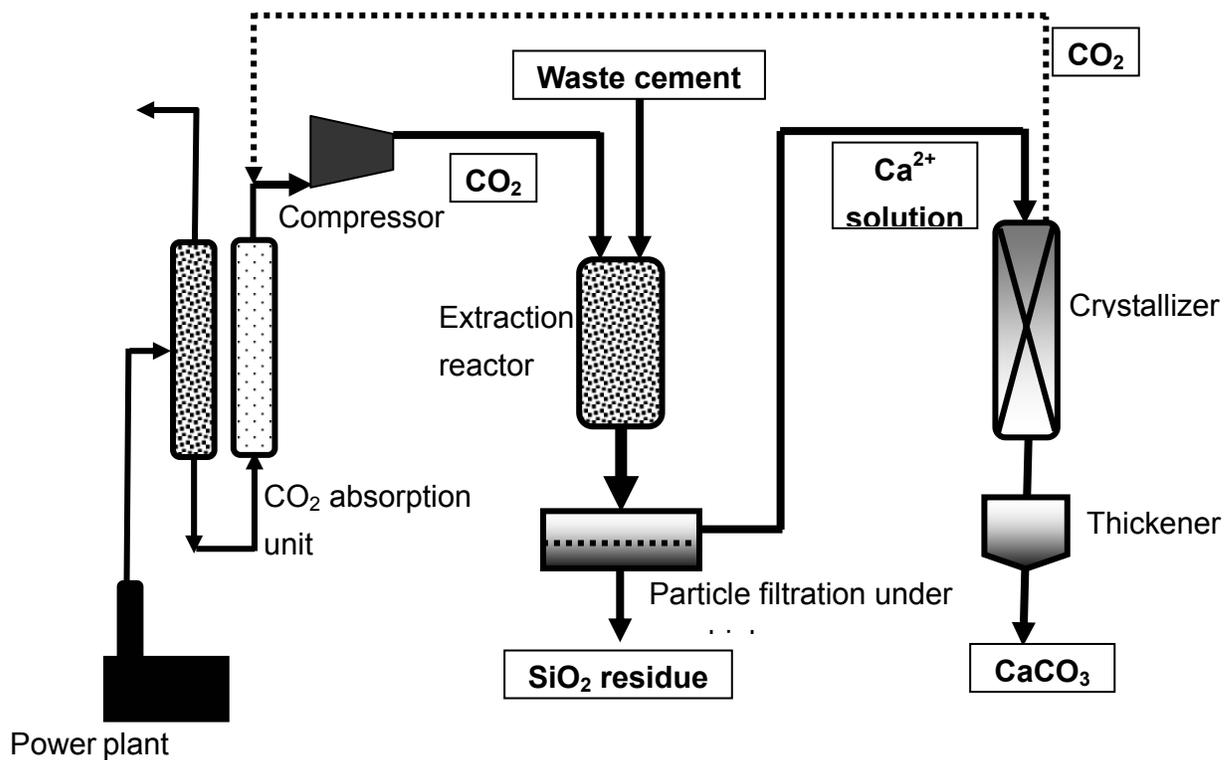


Figure 8 Schematic flow diagram for the direct carbonation process of waste cement with CO₂.

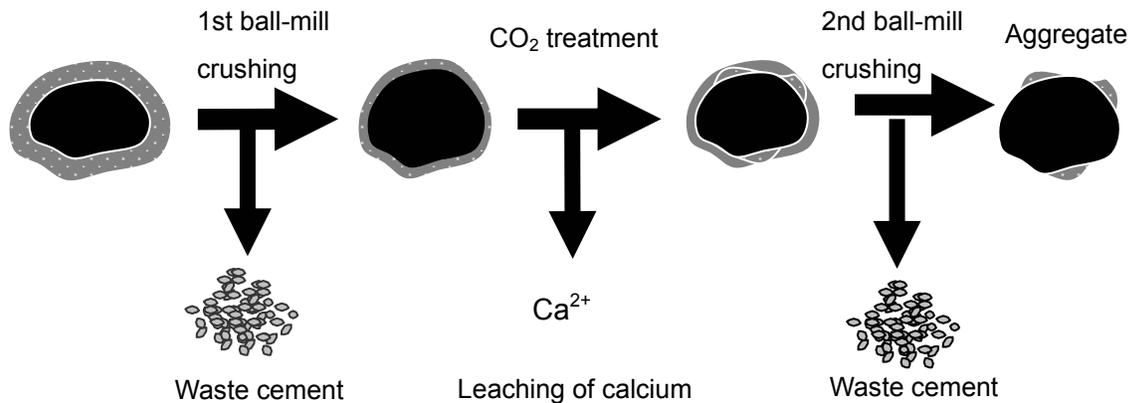
Table 3 Breakdown of the CO₂ sequestration process with direct carbonation of waste cement.

	Power consumption [MW / 100 MW]	Power consumption per ton of CO ₂ [kWh / t-CO ₂]	Operating cost for CO ₂ treatment [USD / t-CO ₂]
CO ₂ capture and separation	5.56	89	7.9
Compression	13.7	223	19.9
Stirring	0.32	5	0.55
Pulverization	6.4	104	9.3
Revenue by selling CaCO ₃	-	-	-15.0
Total	25.9	421	22.6

Recycling process of waste concrete

In the previous section, it is presumed that the waste cement is available as a by-product of a recycling process of waste concrete. However, the recycling process of waste concrete may not necessary be an established process because of difficulty in recovering fine aggregate. Waste concrete is composed of fine aggregate (diameter < 5 mm), coarse aggregate (diameter > 5 mm), and the hydrated cement component. Coarse aggregate can be easily separated from waste concrete with a pulverization treatment. On the other hand, hydrated cement cannot be removed from fine aggregate with a simple mechanical process such as pulverization or crushing. Fine aggregate with cement hydrate cannot be reused as a building material because of high water absorption capacity, which may reduce the building strength. To separate hydrated cement component from fine aggregate, direct carbonation process with high pressure CO₂ could be applied. In such a case, the recycling of fine aggregate from waste concrete and CO₂ sequestration can be realized simultaneously.

The carbonation reaction with high pressure CO₂ was applied for two types of waste concrete samples. Low water absorption capacity is the most important property required for recycled aggregate. In Japan Industrial Standards (JIS), the recycled aggregate should have the water absorption capacity lower than



3.5 % of the aggregate weight. This criteria can be cleared with the CO₂ treatment at 3.0 MPa for a waste concrete particles processed with a mechanical crushing process, of which the initial water absorption capacity was 3.7 %. On the other hand, it was impossible to reduce the water absorption capacity of crushed waste concrete sample. The water absorption capacity was as high as 15.3 %, although after a considerable portion (>80 %) of the calcium content was extracted with high pressure CO₂. However, it was found that the water absorption capacity could be reduced below the JIS standard with a combined treatment process of a high pressure CO₂ treatment and ball-mill crushing as shown in Fig. 9. In the 1st ball-mill crushing process, waste cement component covering fine aggregate could be removed mechanically to generate produce waste cement powder. With the CO₂ treatment, the calcium contents in the remained waste cement covering the aggregate would be leached out. However, some residue with porous structure (mainly SiO₂) would be remained on the surface of the aggregate, which may increase the apparent water absorption capacity. In the 2nd ball-mill crushing, then, the residue would be mechanically removed from the surface of the aggregate.

Figure 9 Conceptual drawing for the aggregate recycling process with a combination treatment of high pressure CO₂ and ball-mill crushing.

Figure 10 shows the change of the water absorption capacity with increasing the CO₂ treatment time. In this experiment, the ball-mill crushing times were fixed at 30 min. The CO₂ treatment for about 120 min is required to achieve the water absorption capacity required in the JIS. Based on the experimental results, a recycling process of aggregates associated with the carbonation of waste cement was designed. The process flow diagram was shown in Figure 11, and the estimation results for the process power consumption were shown in Table 4. From the result, the process can be recognized as a simultaneous process of aggregate recycling and the CO₂ emission reduction.

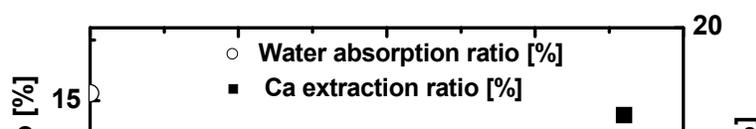


Figure 10 Effect of the CO₂ treatment time on the water absorption capacity.

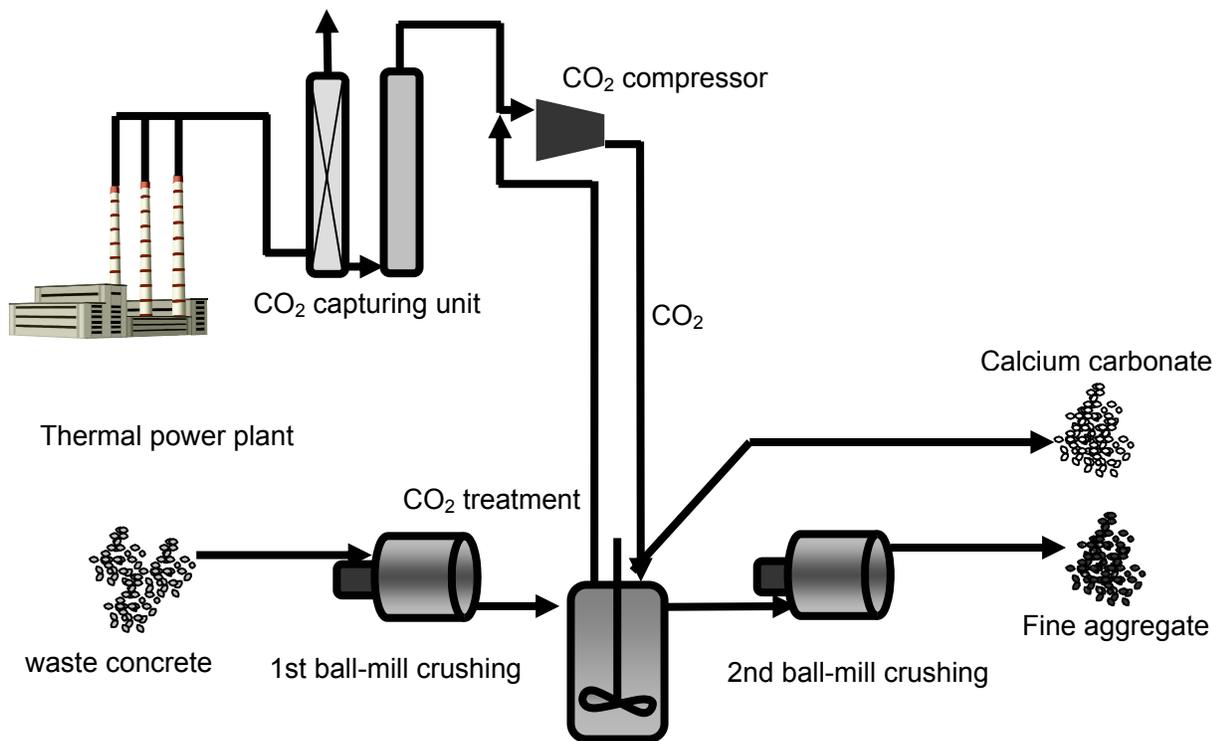


Figure 11 Process flow diagram for the recycling process of fine aggregate from waste concrete.

Table 4 Breakdown of power consumption for the aggregate recycling process with CO₂.

	Breakdown of the power consumption [MJ / ton-aggregate]
CO ₂ capture/separation (heat)	19
CO ₂ compression	60
CO ₂ treatment	214
Ball-mill crushing	96

Total power consumption	369
Net CO ₂ reduction [kg /ton-aggregate]	276

Conclusions

Several kinds of CO₂ sequestration processes have been developed via carbonation reaction, and the processes were evaluated in terms of the power consumption. The proposed processes would be feasible options as a mitigation measure for global warming.

Acknowledgement

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