Development of a new waste cement recycling process by carbonation for flue gas desulphurization process

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Abstract

We propose a new cement recycling process via carbonic acid treatment.   The dependencies of the extraction reaction rate on the ratio of waste cement to water, CO_2 pressure, and the particle size of the raw waste cement particles were investigated experimentally with a laboratory-scale setup.   Calcium carbonate with about 97 % purity was obtained in the precipitation process.   A process simulation was conducted based on the experimental results, and energy consumption and the cost for a model process were estimated.   The cost for the production of 1 metric-ton of $CaCO_3$ for desulfurization of the 500 MW thermal power plant is estimated to be about 120 USD.

Introduction

Concrete is widely used as material for building construction as wood, stone and steel. In concrete, the cement component exists in the form of alkaline compounds such as calcium silicate hydrate (for example, $3CaO \cdot 2SiO_2 \cdot 3H_2O$) and calcium hydroxide ($Ca(OH)_2$). These alkaline compounds could protect the steel frames or reinforcing bars used in concrete buildings from corrosion by acidic atmospheric compounds (*e.g.* carbonic acid). Concrete buildings are dismantled at the end of their lifetime, and the waste concrete generated is construction waste. More than 40 % of the construction waste generated in Japan in the year 2000 was waste concrete, and the rate of waste concrete production has been rapidly increasing in recent years. It is predicted that a huge number of concrete buildings built in the high-growth period of the 1960s and 1970s will have to be demolished in the next 10 to 20 years, and this will generate a tremendous amount of waste concrete. Establishment of processes that can recycle or reuse waste concrete is, therefore, an urgent and important issue.

In previous work, we proposed a new type of process for using the waste cement as a fixation medium for anthropogenic CO_2 emitted from thermal power plants [1]. In that process, waste cement powder is reacted with pressurized CO_2 in a water slurry, and the calcium in the waste cement is leached out into the water phase in the form of calcium ions. When the pressure is reduced, the portion of CO_2 dissolved in the water phase is precipitated out together with the calcium ions as calcium carbonate: the CO_2 is fixed in that form, which is rather stable in terms of the Gibbs free energy. The obtained calcium carbonate can either be

disposed of in appropriate sites or recycled to the cement production industries.

From the viewpoint of the waste cement as a calcium resource, however, the above use as a fixing medium of anthropogenic CO_2 may not be an optimal option. Calcium carbonate, the final product of the proposed process, is a versatile material with a variety of uses. In particular, high-purity calcium carbonate has been in demand for a wide range of applications such as fine chemicals, ceramics and filler. High-purity calcium carbonate

Figure 1 Outline of the recycling process for waste cement. Produced $CaCO_3$ will be sold as a high-purity reagent or as a desulfurization agent.

is also used in flue gas desulfurization processes to produce high-purity gypsum, which is required for the production of gypsum boards. Due to the much higher market price of high-purity calcium carbonate, more economically feasible processes than the fixation of anthropogenic CO_2 could be realized. In this study, the feasibility of a process for producing high-purity calcium carbonate is examined in terms of the energy consumption and the cost, based on experimental laboratory results. In particular, detailed studies were conducted on the process of calcium carbonate precipitation from the leached calcium solution.
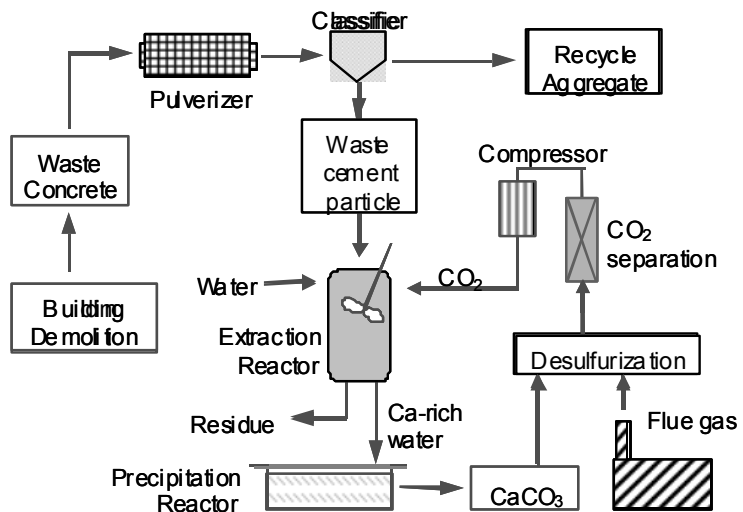
Experimental

Characterization of the waste cement sample

The waste cement sample used in this study was kindly supplied by Tateishi Construction Corp. The sample consists of fine particles obtained as a byproduct of a waste concrete recycling plant after pulverization and classification. The diameter of the waste cement particles was determined by a light scattering method and was found to distribute over the range 10 ~ 200 µm, with a peak at about 25 ~ 40 µm (area based) and about 80 µm (volume based). The weight fraction of calcium was about 27.3 %, based on the elemental analysis. About 11 % of the calcium was found to already be carbonated, based on thermogravimetric measurements with a differential thermal analyzer (ULVAC, TGD-9600).

Calcium extraction experiments

A high-pressure stirring tank vessel reactor was used for the calcium extraction experiments. The inner volume was 500 mL and made of HASTELLOY®, a nickel-based alloy.

A known amount of the waste cement particles was introduced into the reactor under atmospheric conditions, and mixed with a given amount of deionized water. A gaseous CO_2 flow was continuously supplied to the reactor of which the pressure was controlled by a backpressure-controlling valve installed at the downstream side of the reactor. The reactor was immersed in a constant temperature bath, and the reaction temperature was
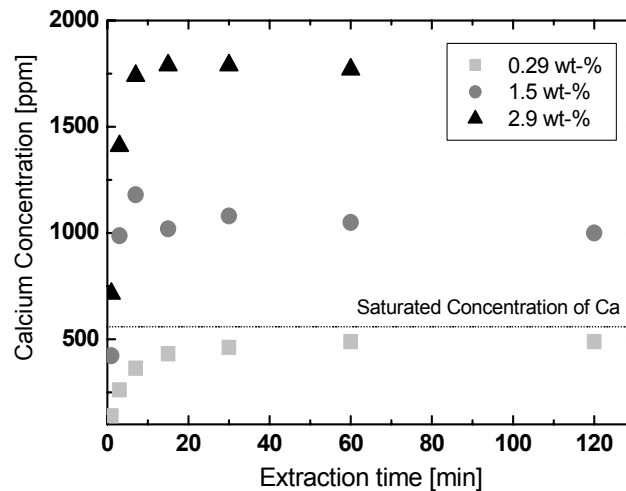

Figure 2 Change in concentration of calcium ions for various initial amounts of waste cement particles. Temperature = 323 K, stirring rate = 900 rpm, and P_{CO2} = 3.0 MPa. The dotted line shows the saturated concentration of calcium under the extraction conditions

controlled with an accuracy of ± 1 K. The stirring in the reactor was carried out by using a two-wing paddle-type fin, and the stirring speed was controlled in the range of 0 ~ 1,000 rpm.

Small portions of the reactor content were sampled at certain intervals during the extraction experiments, through a sintered metal filter with 5 μm mesh. The calcium content of the filtered solution was determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Hitachi, P-4010).

The apparent extraction rates were found to be dependent on the following operating conditions: the weight ratio of waste cement to water (C/W ratio), the temperature, the CO_2 pressure (p_{CO2}), and the average particle size. Figure 2 shows the time course of the calcium concentration in the solution phase for various initial C/W ratios at a fixed stirring speed (900 rpm), temperature (323 K) and p_{CO2}(3.0 MPa). In all cases, the calcium concentration increased rapidly during the initial stage of the reaction, up to about 10 min, and after that the concentration leveled off or decreased slightly. The increase in the rate of calcium ion leaching into the solution phase during the initial stage was greater for the case with the larger C/W ratio. The dotted line in Figure 2 indicates the thermodynamic solubility of the calcium ions corresponding to the present experimental conditions. For conditions with a higher C/W ratio, the solution phase was supersaturated with calcium ions even at a very early stage, and throughout the extraction experiment up to about 120 min. On the other hand, for the case with the lowest C/W ratio (0.29 wt. %), the solution phase never reached supersaturated conditions.The initial extraction rate was found to increase with an increase in the CO_2 pressure. The increase in the extraction rate with increasing CO_2 pressure could be explained in terms of the increasing solubility of calcium ions under high-pressure CO_2 conditions, which would result in the increase in the driving force of the extraction. The initial extraction ratio was found to increase when the average size of the waste cement particles

was decreased [1]. This is because the surface area available for the extraction reaction increases with a reduced particle size. The temperature effect was complicated, and no clear trend was observed for the initial extraction rate over the temperature range studied (303 K to 333 K) [1]. This is because the opposing effects of the increasing temperature, the thermodynamic effect (lower calcium solubility) and the kinetic effect (higher extraction reaction rate) are involved in the apparent extraction rate of calcium ions.

Precipitation of the calcium carbonate

The precipitation reaction step is of primary importance for producing high-purity calcium carbonate. Detailed experimental studies in the present work, therefore, focus on the effects of the operating conditions on the precipitation reaction rates as well as on the purity of the calcium carbonate produced.

All the precipitation reaction experiments were carried out using the aqueous solution obtained from the extraction reaction. The solution obtained from the extraction reaction with given extraction conditions was transferred to the precipitation reactor after filtration through a sintered metal filter of 5 μm mesh. The precipitation reactor is a vessel with a 300 mL inner volume made of reinforced glass. The precipitation

Figure 3   Influence of amount of seed crystal on time course of calcium ion concentration in the solution. Initial solution volume = 200 ml, precipitation temperature = 303 K, stirring rate = 500 rpm, partial pressure of CO_2 = 0.2 MPa. The dashed line in the graph shows the saturation concentration of Ca^{2+} under these conditions, calculated using thermodynamic considerations.

reaction is initiated by reducing the CO_2 pressure or increasing the temperature. The rate of calcium carbonate precipitation was determined by monitoring the concentration of calcium ions in the solution at certain intervals; a small portion of the solution was sampled with filtration (5 μm mesh), and the calcium concentration was determined by ICP-AES (Hitachi, P-4010).

After a given period of the precipitation reaction, the entire reactor content was taken out and quickly filtered. The chemical composition of the particles remaining on the filter was analyzed by a thermogravimetric method with a differential thermal analyzer (Shimadzu, DTG-60H). The thermogravimetric analysis indicated that the content of precipitated $CaCO_3$ was larger than 97%. These results indicate that high-purity $CaCO_3$, which is suitable for use in the desulphurization process for high-purity gypsum production, can be obtained from the
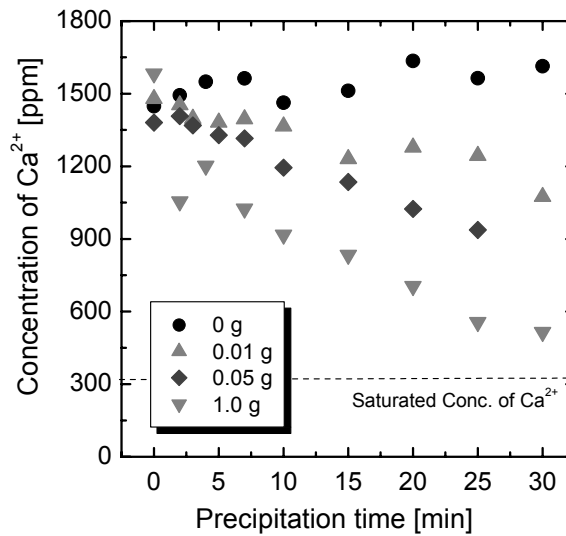
waste cement particles by the present process without any further purification. It should be noted that the addition of seed crystals is essential for producing the high-purity $CaCO_3$ required. Without the addition of seed crystals, the purity of the calcium carbonate is as low as 80%. Thus, the decrease in the calcium concentration in the solution during the precipitation experiments is almost equal to the precipitation rate of calcium carbonate.

The precipitation rate was found to be slightly dependent on the stirring rate, suggesting that no solution phase mass transfer process is involved in the precipitation process for the stirring conditions studied. The rate of $CaCO_3$ precipitation increased with an increase in the temperature. This is because the solubility of calcium ions in water decreases with an increase in the solution temperature, and this increases the driving force for the precipitation. Figure 6 shows the influence of the CO_2 pressure on the precipitation rate. The precipitation rate of $CaCO_3$ decreased with an increase in the CO_2 pressure. This is due to the increase in the solubility of calcium under high CO_2 pressure conditions, and this increases the driving force for the precipitation. Figure 3 shows the influence of the amount of $CaCO_3$ seed crystal on the precipitation rate. An increase in the amount of seed crystal resulted in an increased precipitation rate, due to the increase in the surface area for crystallization. The above results on the influence of the operating conditions are consistent with a general characteristic of crystallization from solutions; i.e. that a lower solubility and higher surface area enhance the crystallization or precipitation rate of crystals.

Process design and simulation for the desulphurization process

The experimental laboratory results reported above demonstrate that both the extraction reaction and the precipitation reaction can proceed at relatively high rates, and that high-purity calcium carbonate, with a purity as high as 97%, can be produced by this process.

In this section, it is assumed that the present process is used in a process for desulphurization of the flue gas of a coal-fired 500 MW thermal power plant, and process design simulation was carried out to estimate the cost and the energy consumption. The schematic process flow is shown in Figure 1. The amount of $CaCO_3$ required for the wet desulphurization process of a 500 MW coal-fired plant is 5.0 t/h. The amount of waste cement necessary for the desulphurization is 34 t/h when the weight fraction of calcium available for producing $CaCO_3$ in the waste cement is 24.3 %. In addition, application of the present process to the production of ultra-high-purity calcium carbonate for fine chemicals or ceramics is considered, and the cost and energy consumption of this process are evaluated. The process flow is identical to the one shown in Figure 1, except that the high-purity calcium carbonate product (about 97 % purity) is further purified to 99.9 % by redissolution and recrystallization processes. The production rate is assumed to be 1000 metric tons of $CaCO_3$ per year. For both cases, the CO_2 necessary for treating the waste cement would be supplied by the flue gas of the thermal power plant after desulphurization and consequent separation and pressurization.

The energy consumption and cost estimation results for the desulfurization process

are summarized in Tables 1 and 2. The total energy consumption for the $CaCO_3$ production required for the wet desulphurization process of the flue gas emitted from a 500 MW thermal plant was estimated to be about 0.70 MW, and the breakdown of the unit operations are shown in the first column of Table 1. The three main energy-consuming operations were CO_2 capture and separation, CO_2 pressurization, and pulverization and classification of the waste cement. About 95 % of the total energy consumption is attributable to these three operations. The energy required for the extraction and precipitation reactions was almost negligible in comparison to that required for the above operations. The operating cost is about USD 2,490,000 per year, and the most costly operations were industrial waste treatment and transportation (~74 % of the total cost), and waste water treatment (~ 9 %), as well as the above-mentioned energy intensive operations. About 90 % of the total capital cost is for the construction of the waste water treatment plant and a silo for the waste cement. As a result, the cost for the production of calcium carbonate in this example is USD 136 per metric ton. This number is highly competitive with the commercial price of USD 400.

The results for the production of ultra-high-purity calcium carbonate are shown in Table 2. The three main energy-consuming operations are: CO_2 capture and separation, CO_2 pressurization, and pulverization and classification of the waste cement, about 90 % of the total energy consumption is attributable to these. The energy required for the extraction and precipitation reactions was almost negligible in comparison to that of the above operations. The operating cost is about USD 92,000 per year, and the costly operations were industrial waste treatment and transportation (~65 % of the total cost), transportation of the product $CaCO_3$ (~10 %), and waste water treatment (~ 6 %), in addition to the above-mentioned energy intensive operations. About 90 % of the total capital cost is the construction of the waste water treatment plant and the silos for waste cement and calcium carbonate product. The cost for the production of calcium carbonate is USD 323 per metric ton in this case. This is again much lower than the present market price of ultra-high-purity calcium carbonate, USD 10,000 per metric ton.

The cost estimated in this study may still be able to be reduced significantly. The cost for the industrial waste treatment, which is essentially for the residue of the waste cement after extraction, could be reduced if the residue were used as a roadbed material. This would reduce the cost for the production of calcium carbonate for the desulfurization process to about 56 % of the original cost, and that for the ultra-high-purity calcium carbonate production to about 81 % of the original cost. In both cases, these are significant cost reductions. In summary, the present process is a feasible option for producing $CaCO_3$ for the wet desulphurization process of the flue gas of a thermal power plant.

Table 1 Cost and energy consumption for production of $CaCO_3$ needed in the desulphurization process in the 500 MW coal-fired thermal power plant.

	Power consumption [MW]	Cost of operation [10^3 USD/year]	Cost of plant construction [10^3 USD/year]	Cost of $CaCO_3$ production [USD / t-$CaCO_3$]
CO_2 capture and separation	0.20	202	45	8.1
CO_2 pressurization	0.25	148	7.4	5.1
Waste cement pulverizing and classifying	0.22	131	6.6	4.5
Extraction reactor	0.011	6.6	126	4.3
Precipitation reactor	0.008	4.7	6.0	0.6
Silo for waste cement	-	-	650	21.2
Waste water treatment	-	165	835	32.6
Industrial waste treatment and transportation	-	1832		59.8
Total	0.70	2490	1677	136

Table 2 Cost and energy consumption for production of ultra-high-purity $CaCO_3$ for use as a reagent needed in the proposed process in the 500 MW coal-fired thermal power plant.

	Power consumption [MW]	Cost of operation [10^3 USD/year]	Cost of plant construction [10^3 USD/year]	Cost of $CaCO_3$ production [USD / t-$CaCO_3$]
CO_2 capture and separation	0.006	6.6	1.5	8.1
CO_2 pressurization	0.008	4.8	0.24	5.1
Waste cement pulverizing and classifying	0.007	4.3	0.21	4.5
Extraction reactor	0.0004	0.23	4.1	4.3
Precipitation reactor	0.0004	0.23	0.28	0.90
Redissolution reactor	0.001	0.49	9.0	9.5
Reprecipitation reactor	0.001	0.49	0.62	2.0
Silo for waste cement	-	-	83	60
Silo for $CaCO_3$	-	-	24	24
$CaCO_3$ transportation	-	9.5	-	9.5
Waste water treatment	-	5.4	107	112
Industrial waste treatment and transportation	-	60	-	60
Total	0.024	92	230	323

CONCLUSIONS

The proposed process for producing calcium carbonate from waste cement by using pressurized CO_2 is highly promising for flue gas desulphurization in terms of the cost and the energy consumption. In addition, simultaneous reduction of the two waste streams, namely CO_2 and waste cement, could be realized by the proposed process. The total energy consumption for the $CaCO_3$ production needed in the desulphurization process was estimated to be about 0.70 MW per 500 MW of power generation by a thermal power plant, and the cost is about 136 USD/metric ton of $CaCO_3$, which is highly competitive with the market price of $CaCO_3$ (about 400 USD/metric ton for high-purity $CaCO_3$). We also examined the production of ultra-high-purity $CaCO_3$. In this case, the total energy consumption for $CaCO_3$ production was estimated to be about 0.024 MW per 500 MW of power generation by a thermal power plant, and the cost is about 323 USD/metric ton of $CaCO_3$.

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