Doctoral Thesis

Development of a new total recycling process of waste concrete with a carbonic acid treatment

（二酸化炭素処理によるコンクリート廃棄物のトータルリサイクル技術開発）

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1. Introduction

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1. Introduction

In this first chapter, the amount of waste concrete generation and the proportion of total wastes is illustrated, and existing techniques for waste concrete recycling are overviewed. The problems related to waste concrete recycling and the need for new waste concrete recycling processes to be developed are noted.

1.1 The problem of waste concrete treatment in Japan

Figure 1.1 shows a breakdown of the waste generated in Japan in 2003 (Ministry of the Environment, 2004a, 2004b). The amount of general waste was 51.61 Mt and for industrial waste it was 412 Mt, this latter amount being 89% of the total waste generated in Japan in 2003. The portion of "construction waste" in the industrial waste was about 18.2%, just behind "electricity, gas, heat supply, water" (22%), and "agriculture" (22%).

Figure 1.1. The breakdown of waste generated in Japan in 2003

Figure 1.2 demonstrates the amount of byproduct generation in the construction industry and its breakdown in Japan. The upper area shows data for 1995 and the lower that for 2002. In 1995, the construction byproduct generation amount was very large, at 99 Mt, which accounted for 36% (36 Mt) of the industrial waste generated. The final amount for disposal was 41 Mt, of which waste concrete accounted for 32% (13 Mt).

Figure 1.2. The amount construction byproduct generation in Japan, broken down for 1995 and 2002 (Ministry of Land, Infrastructure and Transport, 2004)

As detailed above, the amount of construction waste generated was large, and the final amount for disposal was also large. Thus, in Japan, the "Construction Material Recycling Act" was promulgated in the May 2000. The law obligates the appropriate recycling of specific construction waste (waste concrete, wood, asphalt) that is generated from specific construction materials (concrete, iron, and wood building materials, and asphalt concrete). With the enforcement of this law from 2002 the Japanese situation concerning construction wastes has drastically changed.

In 2002, the total amount of construction byproducts was 83 Mt, and had been maintained at this high level since 1995. Likewise, the amount of waste concrete also did not decrease, and accounted for 42% (35 Mt). However, the final amount for disposal did drastically decrease. In 2002, the amount for final disposal was just 7 Mt, only 17% of that in 1995, and that for waste concrete had decreased to just 0.9 Mt.

Figure 1.3 shows the variations over time of the waste concrete recycling rate and recycling plant (intermediate site) numbers before and after the enforcement of the "Construction Material Recycling Act" was started. In 1995 (before enforcement), the recycling rate was only about 65%; however, this increased to 96% in 2000, and was 98% in 2002 (after enforcement). The number of intermediate sites has also increased from 1,400 (1995) to 2,400 (2002) sites.

Figure 1.3. Variation over time of the waste concrete recycling rate and recycling plant numbers (Ministry of Land, Infrastructure and Transport, 2004)

Figure 1.4 shows in a flow diagram the present method for recycling waste concrete. The size of the waste concrete generated at demolition sites is roughly under 300 mm, and is called "300 mm under" in Japan. The "300 mm under" is crushed and classified to large sized waste concrete with a diameter of 5 ~ 40 mm, or smaller sized particles with a diameter of 0.15 ~ 5 mm (called "5 mm under"), on-site or off-site. These crushed wastes are recycled on-site as backfill material, or sold as a recycled stone or sand, and used as roadbed materials.

Figure 1.4. A flow diagram of present method of recycling waste concrete (from an interview with the Kajima Construction Corporation)

That is to say, the present recycling process uses concrete waste as landfill, which is relatively innocent waste, in the city instead of sending it to a final disposal site. This recycling process is working well because the amount of waste concrete generated is presently in balance with the demand for roadbed material. However, it is predicted that this balance will be destroyed in the near future in Japan.

Figure 1.5 shows a prediction of the waste concrete generated, by the Ministry of Land, Infrastructure and Transport of Japan. The amount has been achieved over the years, however an increase is predicted. This is due to the fact that a large number of concrete buildings built during the high-growth period of the 1960s and 70s will be demolished in the next 10 to 20 years, generating a tremendous amount of waste concrete. In the prediction, even the medium estimate, waste concrete generation will amount to 50 Mt by 2010.

Figure 1.5. Prediction of the waste concrete generation (Ministry of Land, Infrastructure and Transport, 2002)

Contrarily, a decrease in demand for roadbed material is also estimated Because of the expected decrease in new road construction. These complementary situations will result in a large increase in the quantity of waste concrete; therefore, a new process for recycling waste concrete needs to be developed in the near future.

1.2 The types of waste concrete materials

This section summarizes the types of waste concrete materials, and notes the target for this study. Figure 1.6 is a schematic of the types of waste concrete.

Figure 1.6. Schematic of waste concrete types

As seen in figure 1.4, the ongoing process for the recycling of waste concrete produces "large sized waste concrete" and "5 mm under", that is sold as recycled stone and sand, respectively. In the crushing process, the hydrated cement part, which has little strength relative to that of aggregates, is selectively crushed, generating "waste cement particles". The amount of "waste cement particles" is usually small; however, if aggregate recycling from the waste concrete is also conducted, the amount accounts for 30% of total amount of waste concrete. Table 1.1 shows the weight fractions of concrete waste in the treatment process for waste concrete.

Table 1.1. Weight fraction of concrete waste in the waste concrete treatment process

"Large sized waste concrete" has a diameter of 5 ~ 40 mm and contains coarse and fine aggregates and hydrated cement particles. In the ongoing recycling process, this waste accounts for 80% of the total concrete waste; however, this fraction is freely controlled by the conditions of the crushing operation. "5 mm under" is composed of fine aggregates and hydrated cement particles. "Waste cement particles" are gray ash-colored fine powder (~ 200 μm) containing hydrated cement and finely crushed aggregate. When aggregate is recycled from waste concrete, the amount of the "waste cement particles" accounts for 30% of the total amount of waste concrete, and treatment becomes problematic.

1.3 Existing recycling processes of waste concrete

In this section, the present recycling processes for waste concrete are reviewed. Especially, as the depletion of high-quality aggregate resources is severe problem in west Japan; the process for aggregate recycling has been intensively investigated.

1.3.1 The process for recycling stone and sand is by crushing and classifying

Refer to figure 1.4. The target waste is "300 mm under", and recycled stone and sand. The fractions of stone and sand and any byproduct generated in the process are summarized in table 1.1.

1.3.2 Aggregate recycling by a process of crushing and scrubbing

The target waste in this process is "large sized waste concrete", in which coarse aggregate is produced. A byproduct of the process is "5 mm under" and a small proportion of "waste cement particles". The fractions of these byproducts generated are summarized in table 1.1. The mechanism of the recycling process is the separation of aggregate and hydrated cement particles that deteriorate the quality of the recycled aggregate. As a reference, a flow diagram of the recycling process is set in figure 1.7.

Figure 1.7. Flow diagram of aggregate recycling by a process of crushing and scrubbing

In this technique, only coarse aggregate can be recycled as in aggregate recycling using this technique is difficult because of the smaller particle size that lowers the scrubbing efficiency. Tateishi Construction Corporation and Daitou Doboku are two organizations that utilize this recycling technique.

1.3.3 Aggregate recycling by a process of heating and scrubbing

The target waste in this process is "large sized waste concrete" and "5 mm under", and both coarse and fine aggregates are recycled. A byproduct of the process is heated "waste cement particles" at 673 K; its fraction being 30% of the total initial waste concrete weight. The mechanism for the process involves the deterioration by heating the interface of hydrated cement particles and aggregates. Thought the Tokyo Electrical Power Corporation and the Shimidzu Construction Corporation developed this process at 2001, the technique is still at a the research stage due to its high energy use and costs.

The above-mentioned current recycling processes for "large sized waste concrete" and "5 mm under" are summarized in table 1.2.

Table 1.2. Existing recycling processes for "large sized waste concrete" and "5 mm under"

1.3.4 Recycling processes for "waste cement particles"

Several recycling processes have been investigated for "waste cement particles" recycling. However these processes have technological and economical problems, and so have not yet been applied in practically adapted yet. The application of "waste cement particles" to a cement alternative has also been examined; however, it was found that "waste cement particles" no longer possess sufficient strength (K. Yamamoto, et al., 1998) even after heating at 1273 K (S. Hatanaka, et al., 1997). Further, the application of "waste cement particles" as cement raw materials was examined by Arai et al., who determined that the addition of up to 20% of "waste cement particles" did not influence the quality of recycled cement. However, it is difficult to consider that "waste cement particles" contribute to the strength of concrete produced from recycled cement. Kojima et al. (1993) noted that "waste cement particles" only play a role as an alternative to clay as a cement raw material. The current recycling processes for "waste cement particles" are summarized in table 1.3.

Table 1.3. Existing processes for recycling "waste cement particles"

1.4 Objective of the research

Japan is predicted to generate increased quantities of waste concrete in the future. It is especially difficult to recycle "5 mm under", and "waste cement particles" utilizing the existing recycling processes, and so a new recycling process that can recycle these wastes is needed in the near future. In this study, I focused on "waste cement particle" recycling because the development of such a recycling process is more necessary for concrete recycling. The objective of this research is to propose a novel recycling process for "waste cement particles".

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Appendix I

I.1 What is concrete?

Concrete is widely used as a building material and is composed of coarse and fine aggregates, cement, water and some additives. Figure I.1 shows the profile of general concrete, and figure I.2 shows the general composition rate (Society of Inorganic Materials, Japan, 1995). The cement fraction of concrete is said to be about 20%. Aggregates account for a large part of the concrete volume and weight.

Figure I.1. Profile of general concrete (from Wikimedia Commons)

Figure I.2. General composition of concrete (ref. Society of Inorganic Materials, Japan, 1995)

I.2 What is cement?

Cement is an inclusive term that represents hydraulic calcium silicate. Portland cement, which is industrially produced, is widely used as a building material in the form of concrete mixed with water and aggregates. Cement as we understand it today was an innovation of the Englishman Joseph Aspdin in 1824.

I.2.1 Types and production process of cement

General cement is produced from ingredients such as limestone ($CaCO_3$), silica rock (SiO_2), clay ($Al_2O_3 \cdot 2\ SiO_2 \cdot H_2O$), and iron oxide ($Fe_2O_3$). These raw materials are crushed, mixed, and heated at about 1700 K to obtain cement clinker. The cement clinker is then crushed with gypsum ($CaSO_4 \cdot 2H_2O$), which is added to control the hydrated reaction rate, to produce cement powder. There are several types of portland cements with different chemical compositions, as shown in table I.1

Table I.1. The types of Portland cement and chemical compositions (Society of Inorganic Materials, Japan, 1995)

There are not large differences in the elemental compositions between each cement type. Calcium oxide (CaO) accounts for the largest part (65%) of the cement weight, followed by silica oxide (SiO_2) which accounts for 22 ~ 26%. However there are great differences in the various compositions of the hydraulic chemicals between each type, and due to these differences each type of portland cement has a different performance.

I.2.2 Amount of cement produced and the total accumulated

The upper bound for cement consumption is said to be 750 ~ 800 kg/person/year; a level that many advanced industrial countries have already reached. Figure I.3 shows the amount of cement produced in Japan (Japan Cement Association HP), and table I.2 shows the amounts cement production and accumulation per person (Youichi Kaya, Ohmsha, editor, 1999). Table I.3 shows the amount of cement produced worldwide (Youichi Kaya, Ohmsha, editor, 1999). Mainland China produces the largest amount of cement, about 500 Mt annually. The amount produced is now only 400 kg/person/year, though this is predicted to increase with China's further

Figure I.3. The amount of cement produced in Japan

Table I.2. The amount of cement used and accumulated per person

Table I.3. The amount of cement produced worldwide

I.2.3 The hydrated reaction of cement

The hydraulic chemical compounds in cement react with water and are hydrated, giving the physical strength. The driving force of this hydration reaction is the difference of the solubility between powdered cement compounds and hydrated cement compounds

(Society of Inorganic Materials, Japan, 1995). The main component of cement is C_3S ($3CaO \cdot SiO_2$), and its hydration reaction is as follows (F. Tomosawa, 1974; S. Takagi, 1974; T. Mori et al.; 1972).

$$2[CaO \cdot SiO_2] + 6H_2O \rightarrow [3CaO \cdot 2SiO_2 \cdot 3H_2O] + 3Ca(OH)_2 \qquad \text{(R. I.1)}$$

The high alkalinity of hydrated cement is derived from calcium hydroxide ($Ca(OH)_2$) that is produced in the above reaction.

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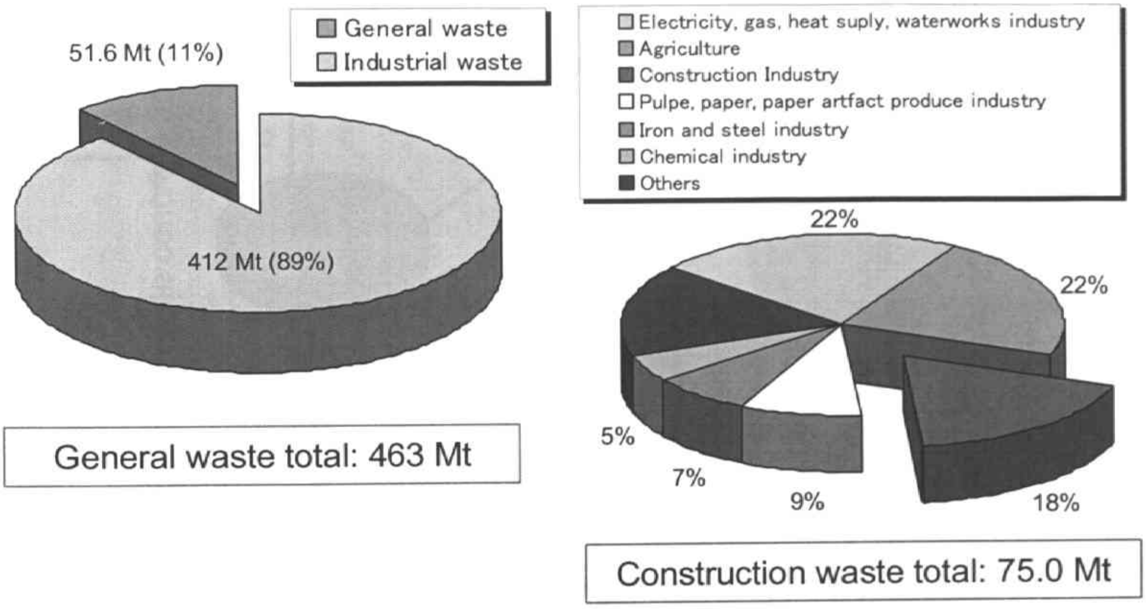

Figure 1.1. The breakdown of waste generated in Japan in 2003

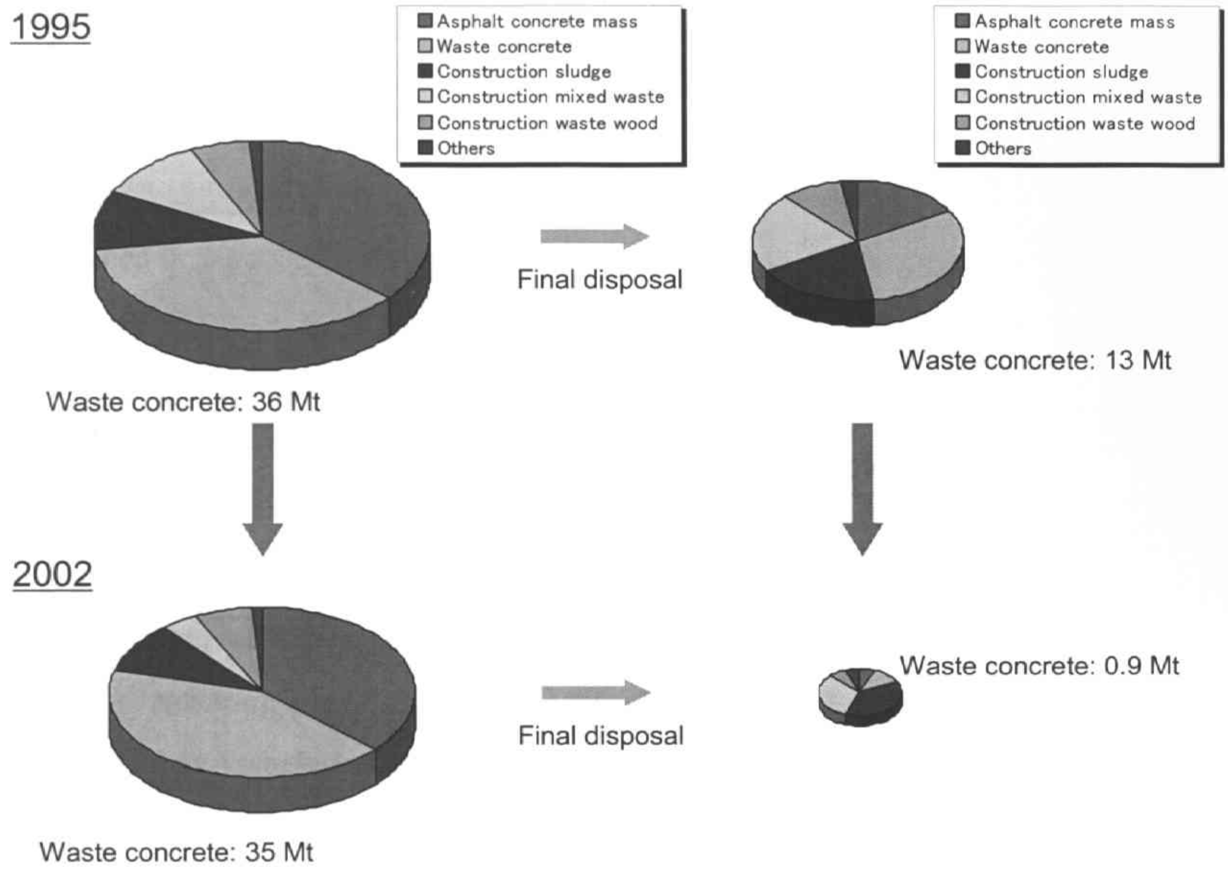

Figure 1.2. The amount construction byproduct generation in Japan, broken down for 1995 and 2002 (Ministry of Land, Infrastructure and Transport, 2004)

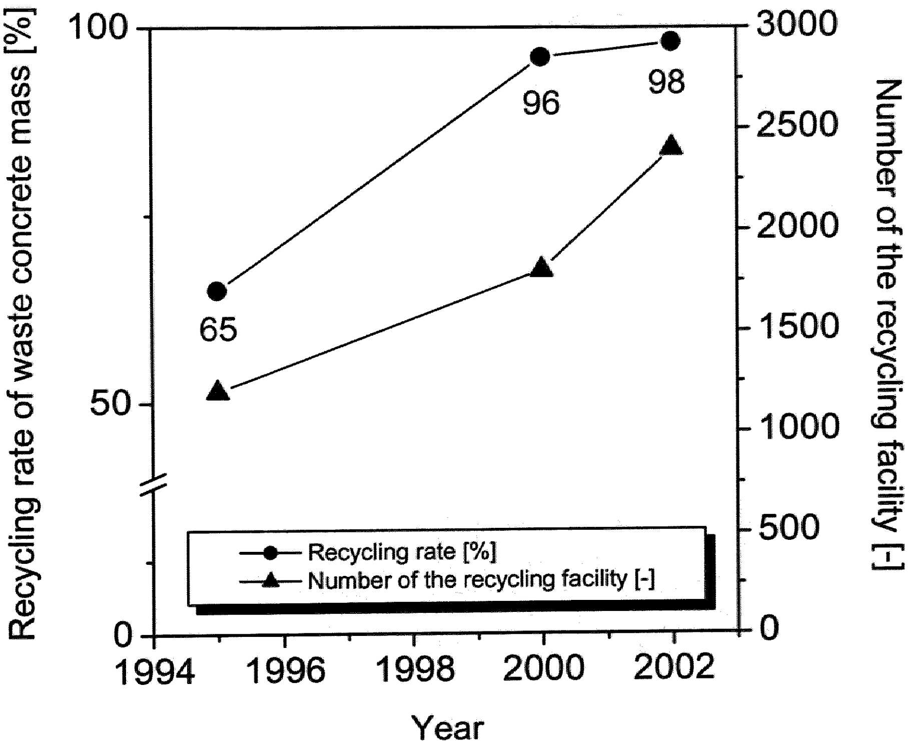

Figure 1.3. Variation over time of the waste concrete recycling rate and recycling plant numbers (Ministry of Land, Infrastructure and Transport, 2004)

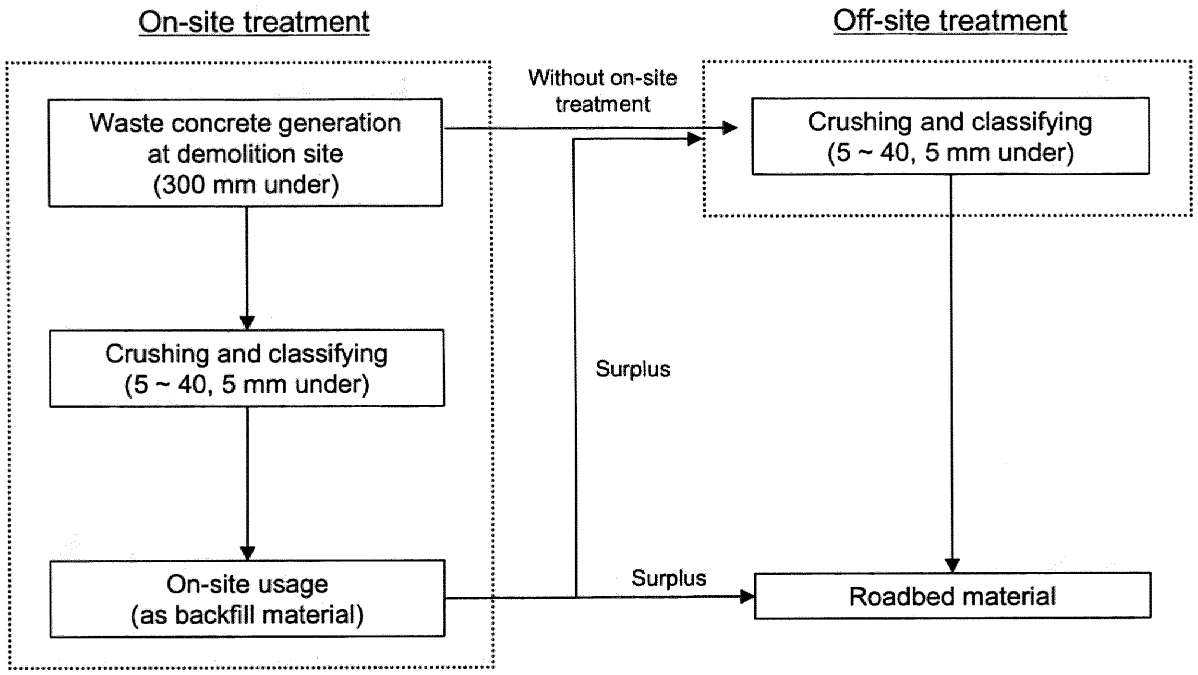

Figure 1.4. A flow diagram of present method of recycling waste concrete (from an interview with the Kajima Construction Corporation)

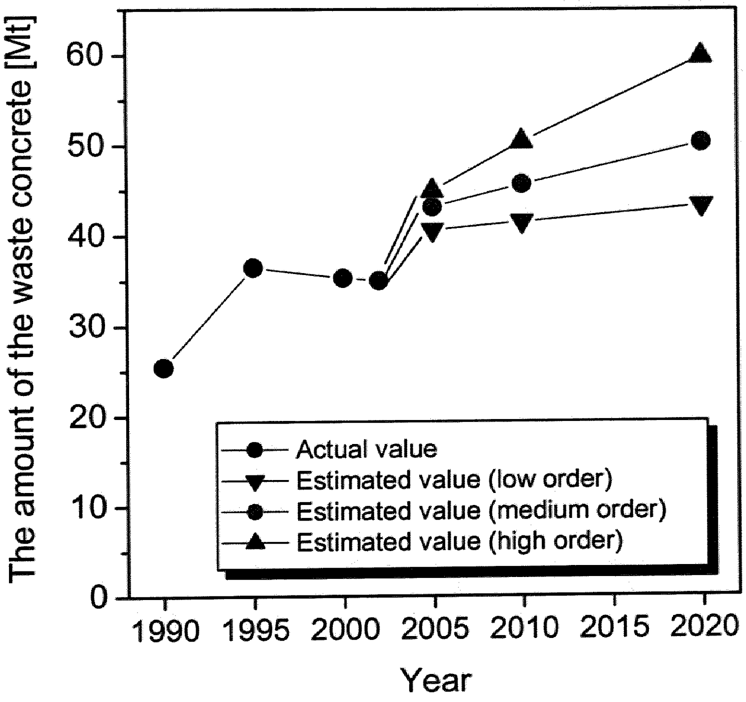

Figure 1.5. Prediction of the waste concrete generation (Ministry of Land, Infrastructure and Transport, 2002)

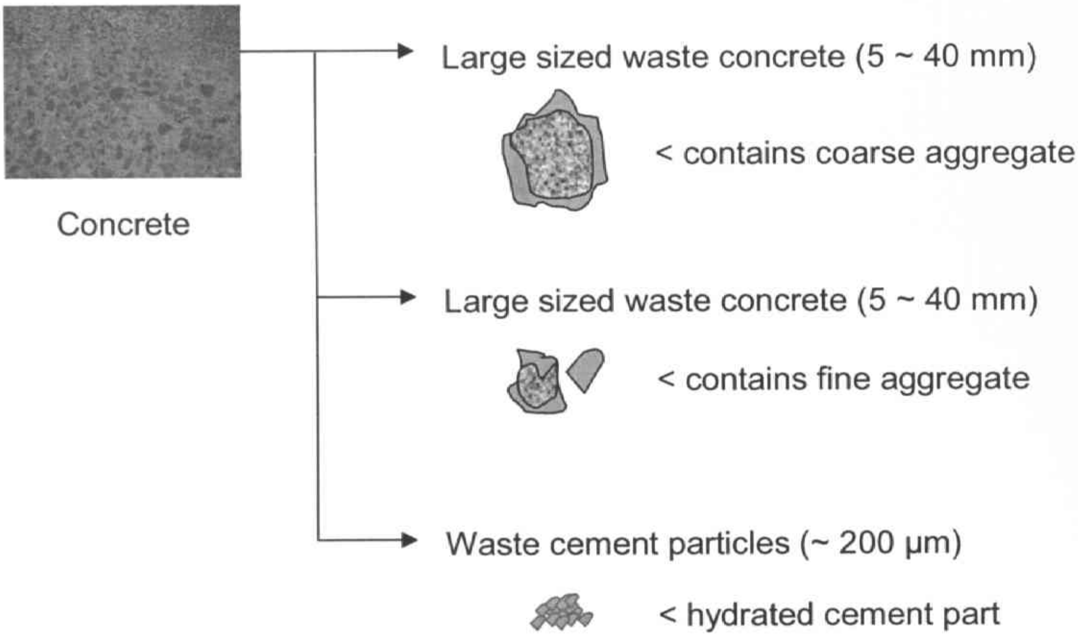

Figure 1.6. Schematic of waste concrete types

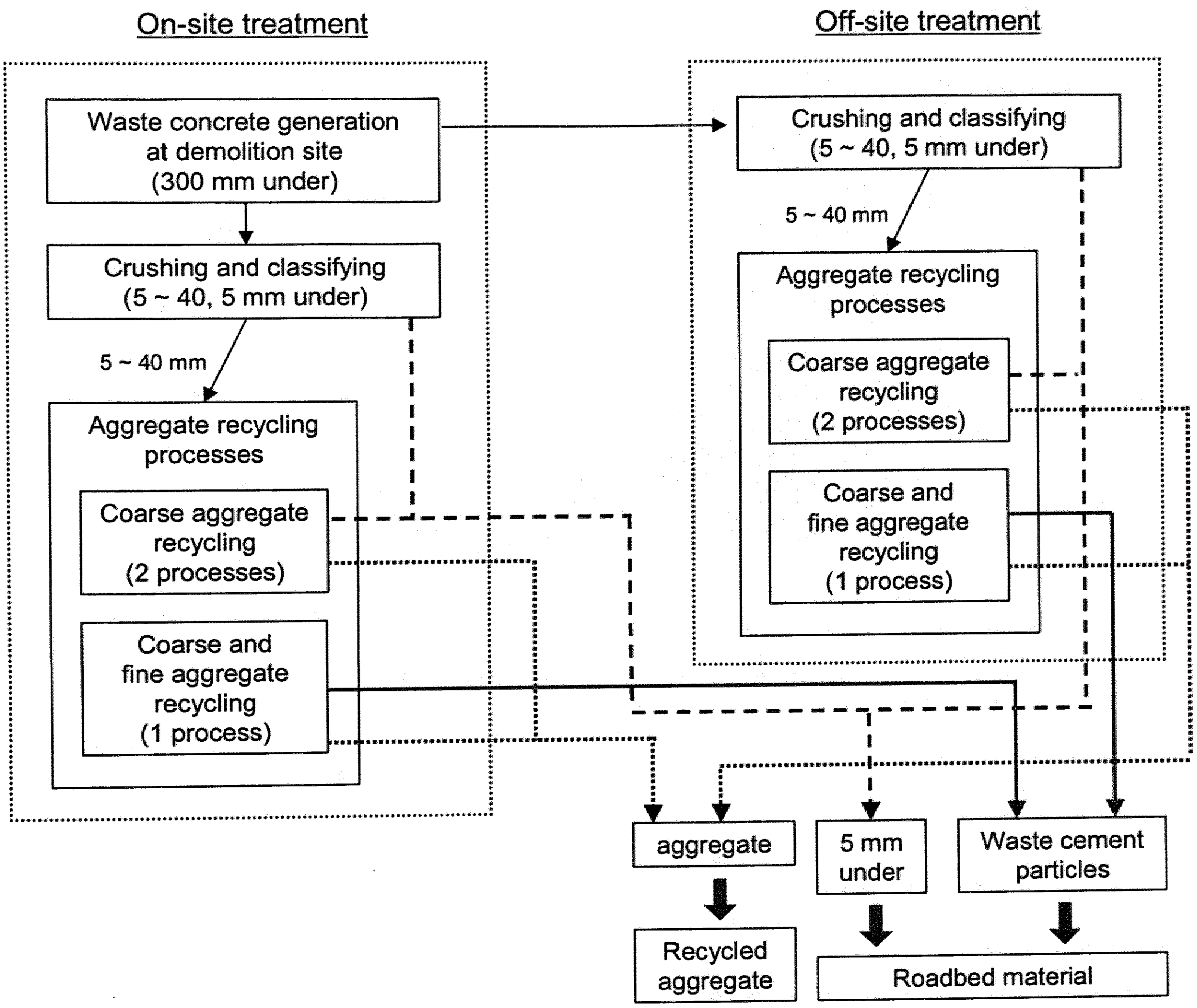

Figure 1.7. Flow diagram of aggregate recycling by a process of crushing and scrubbing

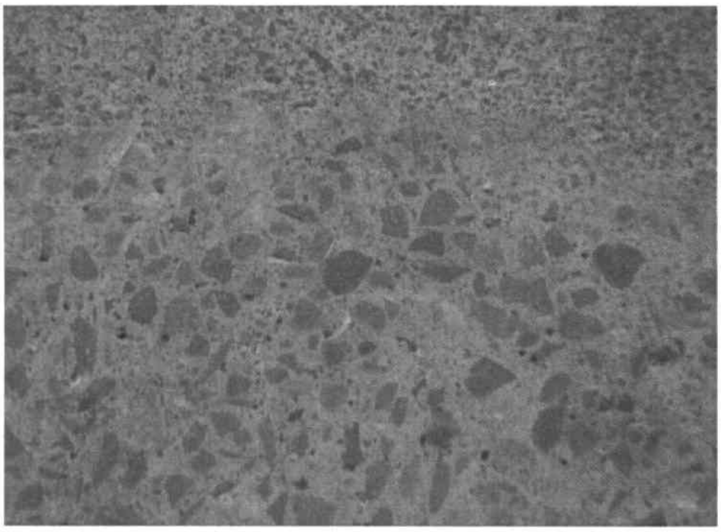

Figure I.1. Profile of general concrete (from Wikimedia Commons)

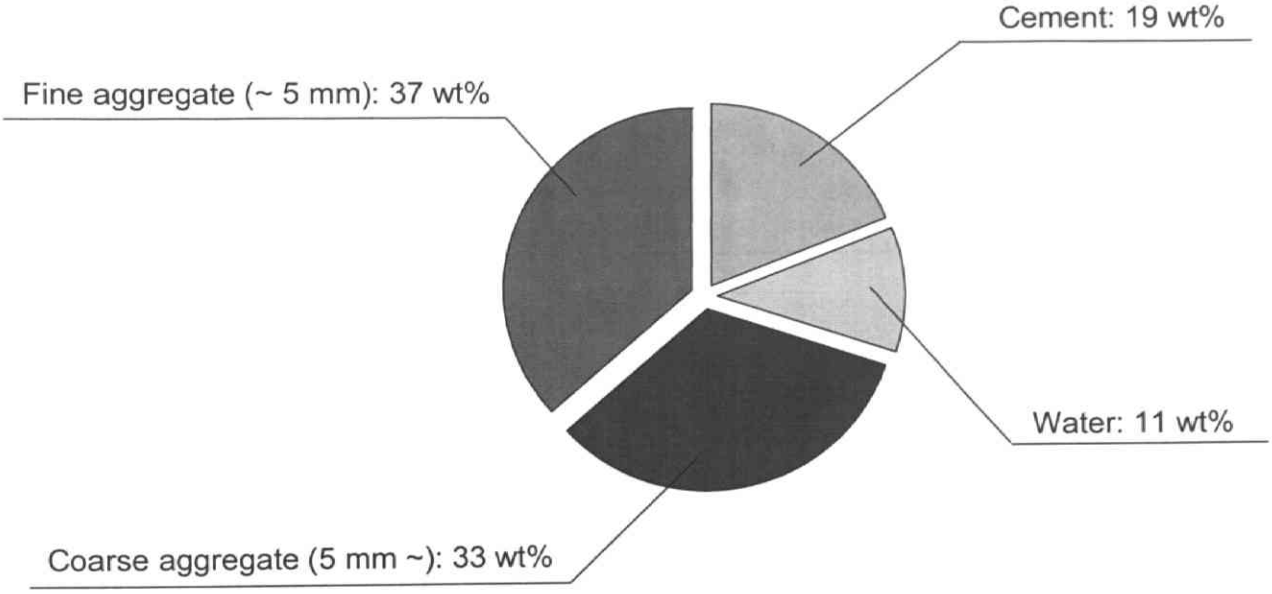

Figure I.2. General composition of concrete (ref. Society of Inorganic Materials, Japan, 1995)

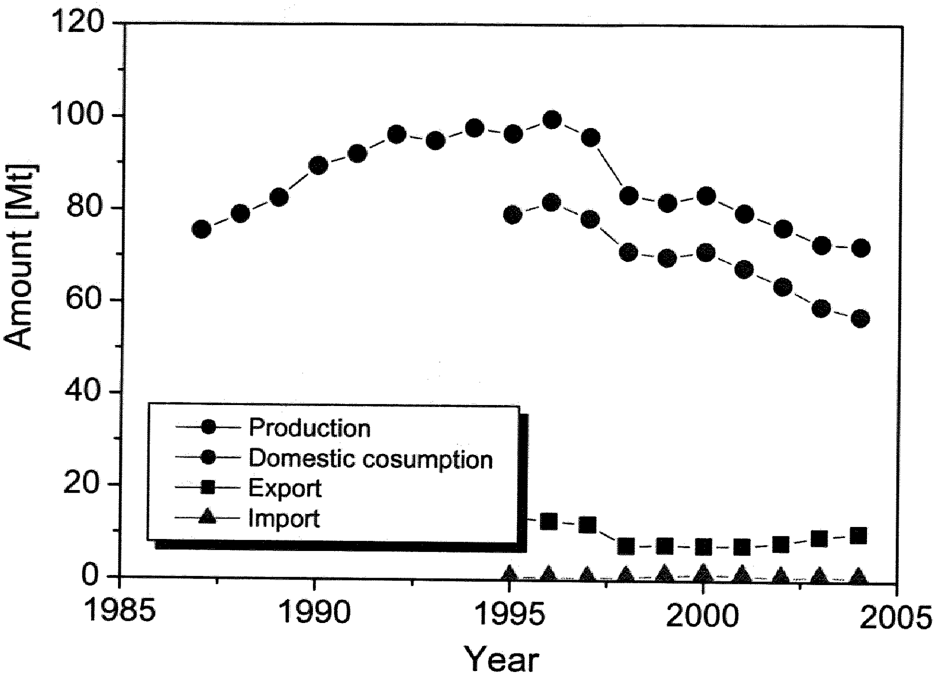

Figure I.3. The amount of cement produced in Japan

Table 1.1. Weight fraction of concrete waste in the waste concrete treatment process

Treatment		Recycled aggregate	5 mm under	Waste cement particles
Crushing and classifying		80% (5 ~ 40 mm)	20%	-
Aggregate recycling process (Crushing and scrubbing)	Coarse aggregate recycle	30%	70%	-
	Coarse and fine aggregate recycle	55%	20%	25%

Table 1.2. Existing recycling processes for "large sized waste concrete" and "5 mm under"

Recycling method	Product	Application	Byproduct	Remarks
Crushing and classifying	Recycled stone (5 ~ 40 mm) Recycled sand (~ 5 mm)	Roadbed materials	Waste cement particles	Present method
Crushing and scrubbing	Recycled coarse aggregate	Concrete	Waste cement particles	Fine aggregate can not be recycled, High cost
Heating and scrubbing	Recycled coarse / fine aggregate	Concrete	Waste cement particles	Necessity of heat, High cost

Table 1.3. Existing processes for recycling "waste cement particles"

Recycling method	Product	Application	Byproduct	Remarks
Crushing	Recycled cement	Cement	-	Strength is not enough
Crushing and heating	Recycled cement	Cement	-	Strength is not enough

Table I.1. The types of Portland cement and chemical compositions (Society of Inorganic Materials, Japan, 1995)

	Elemental composition [wt%]						Chemical composition [wt%]				
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
Ordinary Portland cement (PC)	65.0	21.9	5.3	3.2	1.2	1.9	52	23	9	10	3
Early-strength PC	65.6	21.0	4.9	2.9	1.2	2.7	63	13	8	9	5
Moderate-heat PC	64.8	23.8	3.8	4.0	1.0	1.6	46	33	4	12	3
Sulfate resisting PC	65.2	23.6	3.4	4.0	0.9	1.7	53	28	2	12	3
Low-heat PC	62.2	26.0	3.0	3.1	0.9	2.3	24	56	3	9	4
White PC	65.4	21.8	4.5	0.2	0.5	2.5	63	15	12	1	4

Table I.2. The amount of cement used and accumulated per person

	China	Japan	Korea	US	Russia
Accumulated amount [Mt]	2,483	4,551	649	3,654	3,941
Consumed amount [kg/person]	654	388	1318	341	184

Table I.3. The amount of cement produced worldwide

	China	Japan	Korea	US	World total
1985 [Mt]	146	73	20	71	960
1990 [Mt]	210	84	34	70	1,148
1995 [Mt]	475	91	55	80	1,443
Composition ratio (1995) [%]	32.9	6.3	3.8	3.9	100

2. Proposal for a new waste concrete recycling process with carbonic acid treatment

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2. Proposal for a new waste concrete recycling process with carbonic acid treatment

2.1 Proposal for a new waste concrete recycling process

The new recycling process consists of two steps:

(I) Calcium (Ca) extraction from hydrated cement particles in concrete waste using carbonic acid and solid-liquid separation (under high pressure carbon dioxide (CO_2)).

(II) Calcium carbonate ($CaCO_3$) precipitation (under low pressure CO_2).

Through the above treatment, hydrated cement particles in concrete waste are recycled to sand and $CaCO_3$, the raw material of cement. Aggregate contained within concrete waste is not affected by carbonic acid.

Because hydrated cement consists of alkali compounds, such as calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate ($n\mathrm{CaO}\cdot m\mathrm{SiO_2}\cdot l\mathrm{H_2O}$), it is expected that the hydrated cement component of concrete waste easily reacts with acid, and so the calcium contained within concrete is extracted. Since the aggregate portion of waste concrete and the silicate portion of hydrated cement do not dissolve in acidic conditions, these components are recoverable as solid materials. Extracted calcium is precipitated as $CaCO_3$ under low CO_2 pressure conditions. To make a difference in calcium solubility between steps (I) and (II), the CO_2 pressure swing method is adapted.

2.2 Thermodynamic considerations

In this section, the proposed recycling process is examined from a thermodynamic viewpoint. Figure 2.1 illustrates the simplified relationship of the chemical potentials of cement related materials.

Figure 2.1. Chemical potentials of cement related materials

Cement, in which the chemical form of calcium is roughly considered as CaO, has a high chemical potential relative to limestone ($CaCO_3$). Thus, a large quantity of energy is required to produce cement from limestone. The free energy change for the hydrate reaction of cement is small relative to this energy, though hydrated cement still has high chemical potential. Thus, the reaction of hydrated cement with CO_2 has a negative free energy change, and spontaneously occurs under natural conditions (the same conclusion is obtained through a more detail discussion that considers the complex composition of hydrated cement). In fact, this reaction generally occurs as concrete deteriorate due to reactions with carbonic acid contained in rain. Thus, ideally, a proposed waste concrete recycling process should not need an energy input to produce $CaCO_3$ from hydrated cement. The process proposed here is considered a very reasonable option for concrete recycling. However, as under natural conditions this reaction occurs very slowly, a method accelerating the change would be needed in a practical recycling process.

Then, calcium solubility in the process is considered from a thermodynamic point of view. The amount of $CaCO_3$ produced depends on two factors; the solubility of calcium ions in the extraction process, and the solubility of calcium ions in the precipitation process. The net production of $CaCO_3$ depends on the difference in solubility between the extraction and the precipitation processes. Figure 2.2 shows the results of thermodynamic calculations of the CO_2 pressure dependence of the solubility of calcium ions at 298 K.

Figure 2.2. Saturated concentration of Ca^{2+} and pH as a function of the pressure of CO_2 and pH at 298 K

Solubility strongly depends on CO_2 pressure; to estimate the saturated solubility of calcium ions in carbonic acid, we assume a Ca-H_2O-CO_2 system. Cement contains many chemical elements, which are considered to be extracted from concrete waste by carbonic acid, the same as for calcium. However, in the estimation, the influence of these other elements on the equilibrium state is ignored because the proportions of calcium, hydrogen and oxygen are very high in hydrated cement. A more detail explanation about the equilibrium calculation method is set out in Appendix II.

2.3 Kinetic considerations

In the previous section, the adequateness of the proposed process was discussed from a thermodynamic point of view. If there was plenty of time to treat concrete waste, it would only be necessary to leave it lain outside so that the concrete waste would spontaneously recycle to $CaCO_3$, sand and aggregate from the carbonic acid contained in rain. However, under present circumstances in Japan such a scheme is not feasible. The amount of waste concrete continues to increase, while there is a predicted decrease in the demand for roadbed material. Further, in Japan there is insufficient landfill capacity for use as final disposal sites. Thus, this proposed process needs to be conducted under accelerated conditions. So it is necessary to measure the treatment rates for each unit in the operation of the proposed process under various operational conditions so that this recycling process can be practically evaluated and adapted. The procedures and results of such measurements are discussed in the next chapter.

2.4 Sociological considerations

In this section, the proposed recycling process is discussed from a sociological viewpoint. Specifically, a summarized outline of waste concrete treatment and carbon dioxide emission problems in Japan is presented.

2.4.1 Problems of waste concrete treatment

The recycling rate of waste concrete in Japan has greatly increased in recent years in parallel with enforcement of the "Construction Material Recycling Law" promulgated in 2000. The amount of waste concrete generated is about 35 Mt per year, of which 98% is reused mainly as a roadbed material in 2002 (Ministry of Land, Infrastructure and

Transport, 2004). However, the current recycling processes have several limitations. Emissions from waste concrete are expected to rapidly increase over the next few decades and reach as much as 50 Mt per year in 2050) due to the demolition of a large number of buildings constructed in the 1970's, Japan's high economic growth period, while the demand for roadbed materials is expected to decline in the future with the reduction of public works projects. As well, there is a serious shortage of dumping sites in Japan; the remaining capacity is estimated to be 12.5 years in 2002 (Ministry of the Environment, 2005). Thus, waste concrete might have problems being recycled or disposed of in near future. On the other hand, since ensuring a supply of high-quality natural aggregate is becoming an important issue with resource depletion accompanied with environment protection regulations, the development of an effective recycling process for waste concrete that gives high quality aggregate that can be reused as a building material has become an urgent issue from both waste management and resource conservation aspects.

2.4.2 Problems of carbon dioxide treatment

Japan must reduce its CO_2 emissions by 6% from 2008 to 2012, based on the emission amount at 1990, under the Kyoto Convention. The process proposed here consumes CO_2 for $CaCO_3$ production. 1 mol of calcium contained in waste concrete reacts with 1 mol of CO_2. The CO_2 consumed contributes to the reduction of atmospheric CO_2 emissions. From the viewpoint of CO_2 sequestration, the proposed recycling process is considered to be a mineral carbonation process utilizing industrial waste. The significance of CO_2 sequestration is highlighted in "Special report on carbon dioxide capture and storage" (IPCC WGIII, 2005). For reference, the relationship between waste concrete and the amount of carbon dioxide emission in Japan is shown in figure 2.3.

Figure 2.3. The relationship between waste concrete and the amount of carbon dioxide emission in Japan

In Japan, it is estimated that 10 Gt of concrete has been accumulated in architectural structures (The Society of Inorganic Materials in Japan, 1995). Generally, waste concrete contains about 10% of calcium elements; therefore, the amount of calcium that can potentially be treated by the proposed process is estimated to be 1 Gt. The amount of waste concrete generation is about 35 million ton per year in 2002 (Ministry of Land, Infrastructure and Transport, 2004). The amount is equivalent to 3.5 Mt of calcium. Against this figure, total CO_2 emissions in Japan in 2003 were estimated to be 1.4 Gt. In the proposed process, 3.5 Mt of calcium could react with 3.85 Mt of CO_2, an amount equal to 0.27% of total CO_2 emissions in Japan. Consequently, there is a more than adequate amount of CO_2 emission remaining in Japan to recycle concrete waste by the proposed recycling process.

2.5 Features of the proposed recycling process

The features of the proposed waste concrete recycling process:

- The hydrated cement portion of waste concrete is recycled to $CaCO_3$ and sand by carbonic acid.
- The aggregate portion of waste concrete is not affected by carbonic acid.
- A clean process that only uses water and CO_2 for recycling.
- The process has a CO_2 emission reduction effect.
- The overall reaction of the recycling process has a negative change of free energy, so that the reaction occurs spontaneously.

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Appendix II Thermodynamic equilibrium calculations for the Ca-H_2O-CO_2 system

II.1 Equilibrium reactions

For thermodynamic equilibrium calculations for the calcium (Ca)-carbon dioxide (CO_2)-water (H_2O) system, the following equilibrium reactions were considered. In the equilibrium calculations, the existence of calcium carbonate ($CaCO_3$) was assumed.

$CO_2(g) + H_2O \Leftrightarrow H_2CO_3^*$: K_1 (R. II.1)

$H_2CO_3^* \Leftrightarrow H^+ + HCO_3$- : K_2 (R. II.2)

$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$: K_3 (R. II.3)

$H_2O \Leftrightarrow H^+ + OH^-$: K_w (R. II.4)

$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$: K_{sp} (R. II.5)

where $K_1 \sim K_{sp}$ is the equilibrium constant for each equilibrium reaction.

II.2 Temperature dependency of the equilibrium constant

For the temperature dependency of the equilibrium constant, an Arrhenius type dependency was assumed in the calculations. Equilibrium constant data were obtained from the literature (W. Stumm and J. J. Morgan, 1996) and are shown in table II.1 and 2, while figure II.1 illustrates the Arrhenius plot for each equilibrium constant. The equilibrium constants at given temperatures that could not be obtained from the literature were estimated from this Arrhenius plot.

Table II.1. Temperature dependence of the equilibrium constants

Table II.2. Temperature dependence of the equilibrium constants for an Arrhenius plot

Figure II.1. Arrhenius plot for equilibrium reactions of the Ca-H_2O-CO_2 system

II.3 Calculations of the equilibrium concentration of each chemical in the Ca-H_2O-CO_2 system

This section summarizes the method for calculations of the equilibrium concentration of each chemical in the Ca-H_2O-CO_2 system.

First, the following relational expressions are given from R. 2.1~2.5.

$$K_1 = \frac{[H_2CO_3^*]}{p_{CO2}} \tag{Eq. II.1}$$

$$K_2 = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \tag{Eq. II.2}$$

$$K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \tag{Eq. II.3}$$

$$K_w = [H^+][OH^-] \tag{Eq. II.4}$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \tag{Eq. II.5}$$

where [A] stands for the concentration in solution of chemical “A”. [$H_2CO_3^*$] is the sum of the concentration of dissolved CO_2 (H_2CO_3 (*l*)) and liquid CO_2 (CO_2 (*l*)). p_{CO2} is the pressure of gaseous CO_2.

From the electrical charge balance in the system,

$$2[Ca^{2+}]+[H^+]=[HCO_3^-]+2[CO_3^{2-}]+[OH^-] \tag{Eq. II.6}$$

In the following calculation, [H^+] concentration is assumed to be known, and we rearrange Eq. II.6 by [CO_3^{2-}]. From Eq. II.5,

$$[Ca^{2+}]=\frac{K_{sp}}{[CO_3^{2-}]} \tag{Eq. II.7}$$

From Eq. II.4,

$$[OH^-]=\frac{K_w}{[H^+]} \tag{Eq. II.8}$$

From Eq. II.3,

$$\left[\mathrm{HCO_3}^-\right]=\frac{\left[\mathrm{H}^+\right]}{K_3}\cdot\left[\mathrm{CO_3}^{2-}\right] \qquad \text{(Eq. II.9)}$$

Substitute Eq. II.9 to Eq. II.2,

$$\left[\mathrm{H_2CO_3}^*\right]=\frac{\left[\mathrm{H}^+\right]^2}{K_2K_3}\cdot\left[\mathrm{CO_3}^{2-}\right] \qquad \text{(Eq. II.10)}$$

Substitute Eq. II.10 to Eq. II.1,

$$p_{CO2}=\frac{\left[\mathrm{H}^+\right]^2}{K_1K_2K_3}\cdot\left[\mathrm{CO_3}^{2-}\right] \qquad \text{(Eq. II. 11)}$$

Then substitute Eq. II.7~9 to Eq. II.6,

$$2\frac{K_{sp}}{\left[\mathrm{CO_3}^{2-}\right]}+\left[\mathrm{H}^+\right]=\frac{\left[\mathrm{H}^+\right]}{K_3}\cdot\left[\mathrm{CO_3}^{2-}\right]+2\left[\mathrm{CO_3}^{2-}\right]+\frac{K_w}{\left[\mathrm{H}^+\right]} \qquad \text{(Eq. II.12)}$$

Rearrange the above equation,

$$\left\{\frac{\left[\mathrm{H}^+\right]}{K_3}+2\right\}\cdot\left[\mathrm{CO_3}^{2-}\right]^2+\left\{\frac{K_w}{\left[\mathrm{H}^+\right]}-\left[\mathrm{H}^+\right]\right\}\cdot\left[\mathrm{CO_3}^{2-}\right]-2K_{sp}=0 \qquad \text{(Eq. II.13)}$$

Since,

$$\left[\mathrm{CO_3}^{2-}\right]=\frac{-\left\{\frac{K_w}{\left[\mathrm{H}^+\right]}-\left[\mathrm{H}^+\right]\right\}+\left[\left\{\frac{K_w}{\left[\mathrm{H}^+\right]}-\left[\mathrm{H}^+\right]\right\}^2+8K_{sp}\left\{\frac{\left[\mathrm{H}^+\right]}{K_3}+2\right\}\right]^{0.5}}{2\cdot\left\{\frac{\left[\mathrm{H}^+\right]}{K_3}+2\right\}} \qquad \text{(Eq. II.14)}$$

From this equation, $[\mathrm{CO_3}^{2-}]$ for a given $[\mathrm{H}^+]$ can be calculated. Further, the concentrations of other chemicals and p_{CO2} for a given $[\mathrm{H}^+]$ can be calculated from Eq. II.7~11 and 14. Figure II.2 demonstrates the saturated concentration of each chemical in the system as a function of pH at 298 K.

Figure II.2. The concentrations of each chemical in the Ca-H_2O-CO_2 system as a function of pH at 298 K (The plotted point in the graph is only a target.)

The saturated concentration of Ca^{2+} and the total amount of CO_2 existing in solution

(ΣCO_2) increases with a decrease of pH in the system. The main chemical form of CO_2 in the system is $H_2CO_3^*$ under acidic conditions (~ pH6.5). From the neutral to the alkali region (pH 6.5 ~ 10), the main chemical form changes to HCO_3^-.

Figure II.3 shows the saturated concentration of Ca^{2+} and pH as a function of the gaseous CO_2 pressure and pH at 298 K. The saturated concentration of Ca^{2+} increases and the pH of the system decreases with an increase of the pressure of gaseous CO_2 supplied to the system.

Figure II.3. The saturated concentration of Ca^{2+} and pH as a function of the pressure of CO_2 and pH at 298 K

Figure II.4 illustrates the saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature for various CO_2pressures. The saturated concentration of Ca^{2+} decreases with an increase of temperature in the system.

Figure II.4. The saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature (CO_2 pressure dependency)

Reference

W. Stumm and J. J. Morgan, 1996, Aquatic Chemistry – Chemical equilibria and rates in natural waters -, John Wiley and Sons, New York, USA.

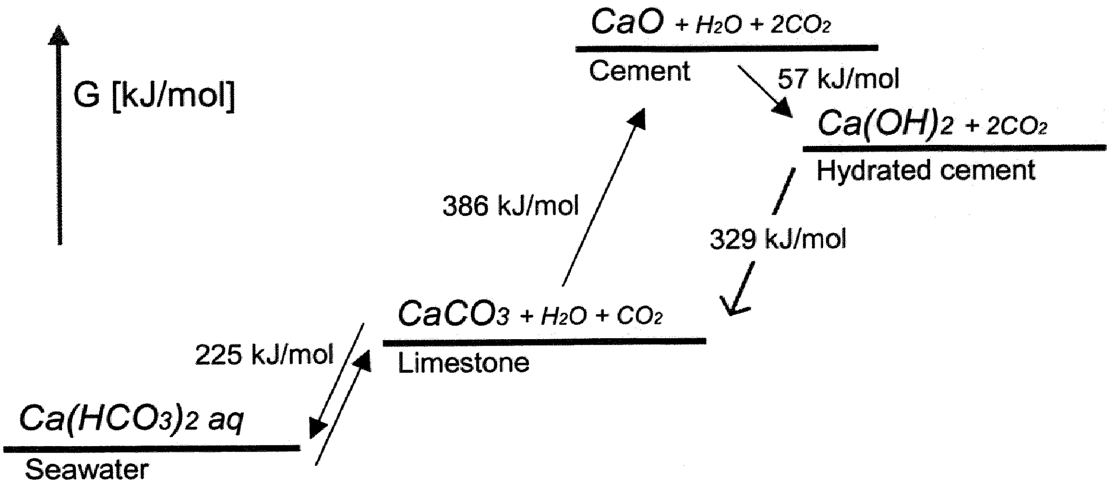


Figure 2.1. Chemical potentials of cement related materials

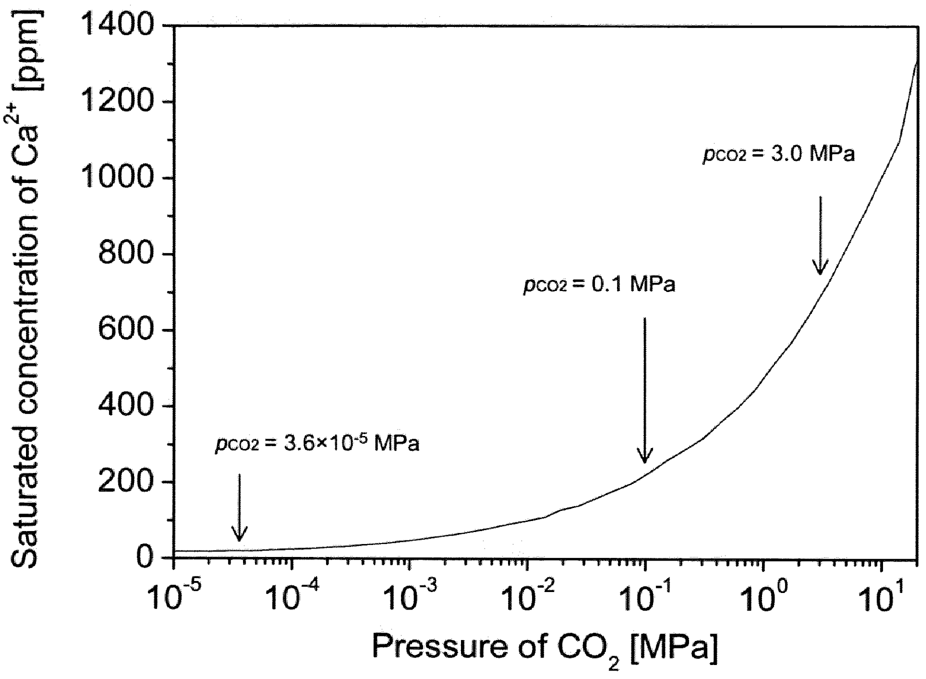


Figure 2.2. Saturated concentration of Ca^{2+} and pH as a function of the pressure of CO_2 and pH at 298 K

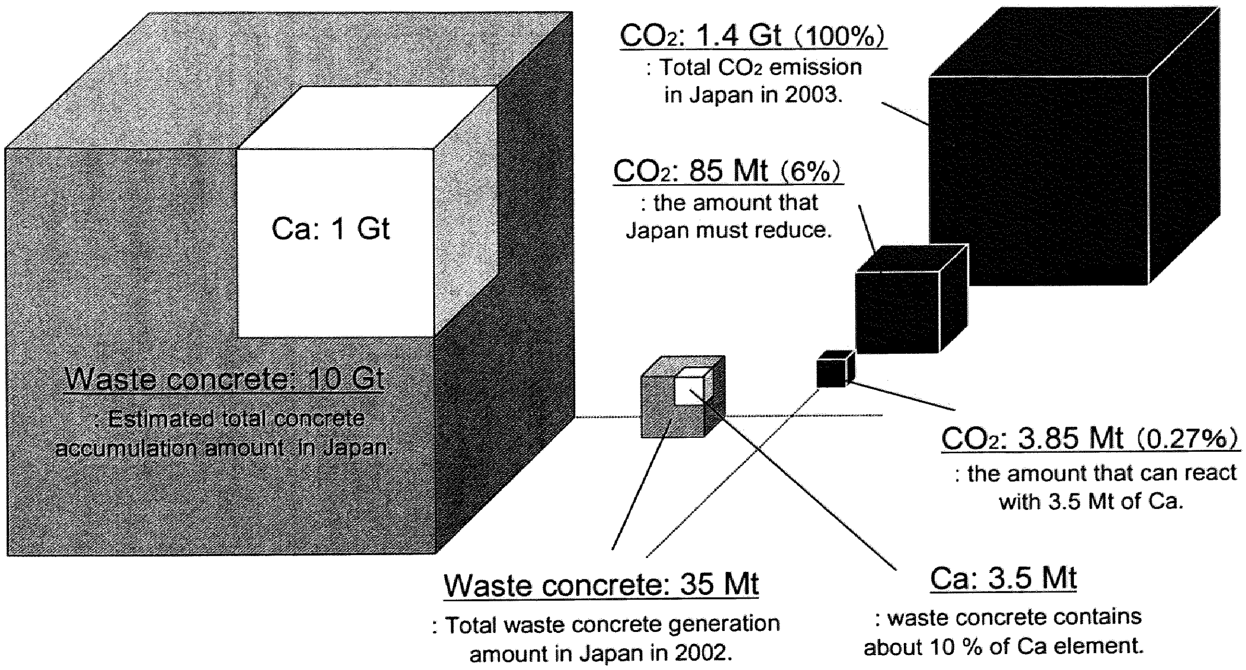


Figure 2.3. The relationship between waste concrete and the amount of carbon dioxide emission in Japan

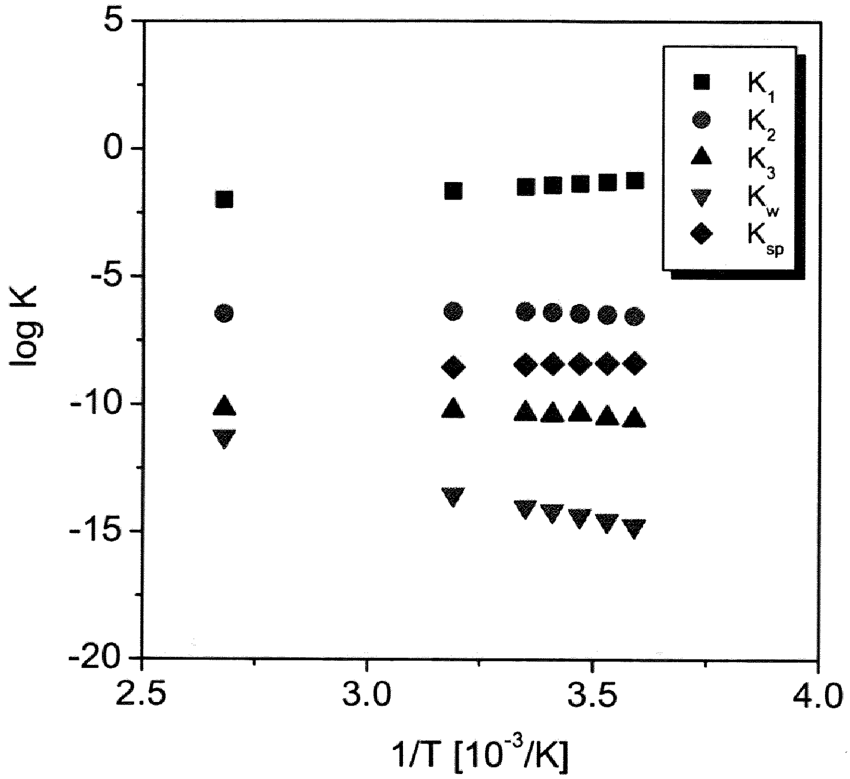


Figure II.1. Arrhenius plot for equilibrium reactions of the Ca-H_2O-CO_2 system

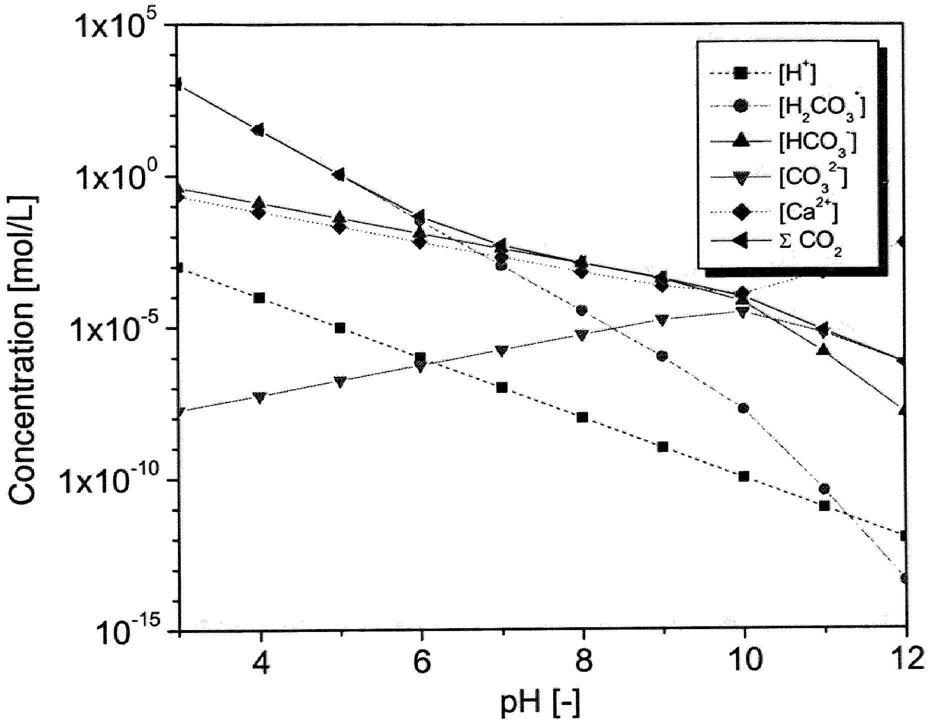


Figure II.2. The concentrations of each chemical in the Ca-H_2O-CO_2 system as a function of pH at 298 K (The plotted point in the graph is only a target.)

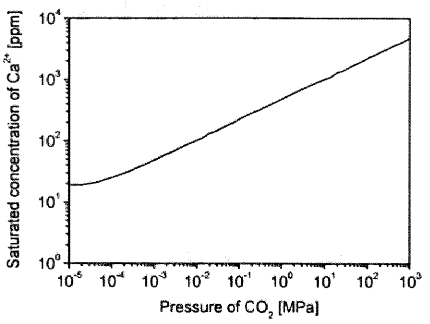
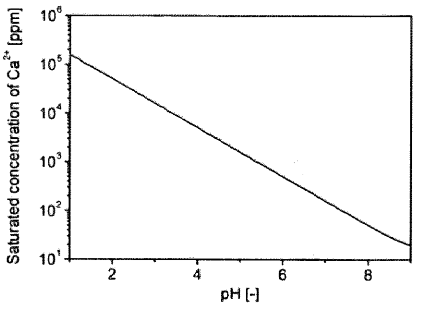
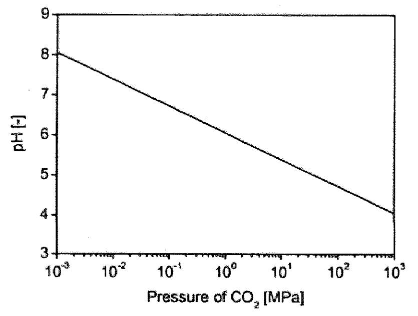
	Pressure of CO_2 [MPa]	pH [-]
Saturated concentration of Ca^{2+} [MPa]		
pH [-]		

Figure II.3. The saturated concentration of Ca^{2+} and pH as a function of the pressure of CO_2 and pH at 298 K

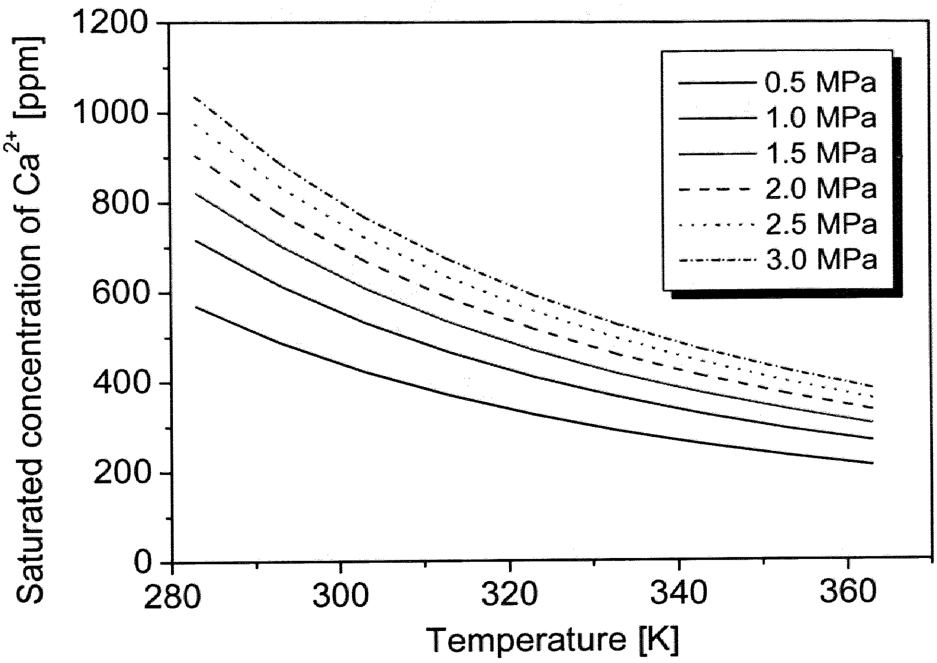


Figure II.4. The saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature (CO_2 pressure dependency)

Table II.1. Temperature dependence of the equilibrium constants (W.Stum and J.J. Morgan, 1996)

	Temperature [K]						
	278	283	288	293	298	313	373
$\log K_1$	-1.2	-1.27	-1.34	-1.41	-1.47	-1.64	-1.99
$\log K_2$	-6.52	-6.46	-6.42	-6.38	-6.35	-6.35	-6.45
$\log K_3$	-10.56	-10.49	-10.34	-10.38	-10.33	-10.22	-10.16
$\log K_w$	-14.73	-14.53	-14.34	-14.16	-14	-13.53	-11.27
$\log K_{sp}$	-8.35	-8.36	-8.37	-8.39	-8.42	-8.53	-

Table II.2. Temperature dependence of the equilibrium constants for an Arrhenius plot (calculated from Table II.1)

	Inverse of temperature [10^{-3}/K]						
	2.68	3.19	3.35	3.41	3.47	3.53	3.59
$\log K_1$	-1.99	-1.64	-1.47	-1.41	-1.34	-1.27	-1.2
$\log K_2$	-6.45	-6.35	-6.35	-6.38	-6.42	-6.46	-6.52
$\log K_3$	-10.16	-10.22	-10.33	-10.38	-10.34	-10.49	-10.56
$\log K_w$	-11.27	-13.53	-14	-14.16	-14.34	-14.53	-14.73
$\log K_{sp}$	-	-8.53	-8.42	-8.39	-8.37	-8.36	-8.35

3. Experimental section

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3. Experimental section

3.1 Characterization of a waste cement sample

As mentioned in chapter 1, only waste cement (the hydrated cement portion of concrete waste) particle recycling by the proposed process is investigated in this study. There are two reasons for this. First, the hydrated cement portion of concrete waste cannot presently be recycled. Second, a feasibility study of a “5 mm under” waste concrete recycling process to fine aggregate can be conducted in a waste cement recycling process (essential differences between these two waste are particle size and the existence of fine aggregate that is not affect by carbonic acid). Thus, for the rest of this report, only waste cement is treated.

3.1.1 The origin

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 at a waste concrete recycling plant after pulverization and classification. In this study, only this waste cement sample was examined. There are 6 main types of Portland cement in Japan (refer table I.1), and the cement water mixing rate could affect the property of the concrete produced. However, ordinary Portland cement makes up a large share of Japan’s concrete usage, and as this sample was obtained from a concrete recycling plan through-putting a large amount of waste concrete, this waste cement sample is considered to be representative of general waste cement material in Japan.

3.1.2 An overview

The waste cement particle used in this study was a gray ash colored fine powder. Figure 3.1 shows an SEM image of a waste cement particle. From this image, it is suggested that the waste cement particle surface has a relatively large surface area.

Figure 3.1. Surface image of a waste cement particle (SEM)

3.1.3 Particle size distribution

The diameter of the waste cement particles was determined by a light scattering method and was found to distribute over a range 10 ~ 200 μm, with a peak at about 10 ~ 30 μm in area (figure 3.2). More detailed results of the particle size measurements are summarized in table 3.1.

Figure 3.2. Particle size distribution of waste cement particles by light scattering, diameter based on particle surface areas

Table 3.1. Light scattering illustration of particle size distribution of the waste cement sample

3.1.4 Composition

The elemental composition of the waste cement particle was analyzed by X-ray fluorescence (JEOL, JSX-3220). A calibration curve method with standard addition was adapted for the measurement. The existence ratios between each metal element were analyzed by the FP method. Consequently, the chemical composition of the waste cement sample was estimated. These results are summarized in table 3.2 and 3.3.

Table 3.2. Elemental content of the waste cement sample

Table 3.3. Estimated chemical composition of the waste cement sample

The main component of the waste cement sample is calcium, having a weight fraction of about 27.3 %. Next to calcium, silicon, iron and aluminum also have large contents. It is considered that the sulfur in waste cement particle is derived from calcium sulfate ($CaSO_4$), which used in cement production. Because the molecular weights of sulfur and calcium are 32.07 and 40.08, respectively, the weight percentage of calcium in the form of $CaSO_4$ to waste cement is estimated to be 0.65 wt% (= 40.08/32.07×0.52). Thus, it is estimated that 2.38 wt% (= 0.65/27.3×100) of calcium in the waste cement sample is $CaSO_4$. The contents of other alkali elements, such as potassium and sodium, were very small (potassium: 0.21 wt%, sodium: not detected).

3.1.5 The carbonated ratio

The sample consists of fine particles obtained as a byproduct in a waste concrete recycling plant after pulverization and classification. The weight of the waste cement sample is about 25 kg. The sample had been preserved in a plastic and paper bag since 1998. The carbonation ratio of the sample was analyzed by thermo gravimetric measurements with a differential thermal analyzer (ULVAC, TGD-9600). Figure 3.3 shows the result of thermal gravimetric analysis of the sample.

Figure 3.3. Weight variation of waste cement particles on heating

A weight decrease was observed with temperature increase. It is considered that the moderate weight reduction in a temperature range from 373 K to 900 K is derived from desorption of water: such as absorbed water, interstitial water in hydrated cement structure, and crystal water. The distinct weight reduction was observed around 1000 K derived from $CaCO_3$ pyrolysis. The weight decrease was 3.4 wt%; thus, the carbonated ratio of calcium in the sample was estimated to be 11.3% (= 3.40×40/44/27.3×100).

Carbonation of waste cement will reduce the potential capacity for CO_2 sequestration. Since the waste cement sample came from dismantled buildings that were several decades old, the calcium content would have been exposed to carbonation by atmospheric CO_2 for a long period of time. The carbonation kinetics of cement in concrete are reported by several authors; in a period of about 3 years, the degree of carbonation is normally limited within several mm thickness from the surface (Houst Y. F.and Wittmann F. H, 2002). It is generally thought that the depth of carbonation is proportional to the square root of the exposure time; after 50 years exposure, the neutralization depth in the concrete is still limited to about 1 cm from the surface. Considering the thickness of concrete used in most buildings, there is limited carbonation and this only occurs near the surface exposed to the atmosphere.

3.2 Calcium extraction experiments from waste cement particles

Although the thermodynamic calculations indicate that it is theoretically possible to convert calcium content in waste cement into $CaCO_3$, the practical conversion rate would largely be determined by reaction kinetic factors. For example, the apparent extraction rates depend on the various operating conditions of temperature, the weight ratio of waste cement to water (C/W ratio), CO_2 pressure (p_{CO2}) and the particle size of the waste cement sample. The kinetic data for the extraction process needs to be determined for the design of the extraction and the precipitation processes. In this section, extraction kinetics are examined through lab-scale experiments.

3.2.1 Experimental apparatus

A high-pressure stirring tank vessel reactor made of HASTELLOY®, a nickel-based alloy with an inner volume of 500 mL was used for the calcium extraction experiments. A schematic drawing of the experimental apparatus is in figure 3.4.

Figure 3.4. Schematic drawing of the experimental apparatus for the calcium extraction experiments

3.2.2 Experimental procedure

A known amount of waste cement particles was introduced into the reactor under atmospheric conditions and mixed with a given amount of ultra high-purity water. A gaseous CO_2 flow was continuously supplied to the reactor. The reactor was immersed in a constant temperature bath to control the reaction temperature to an accuracy of ± 1 K. The reactor was stirred using a two-wing paddle-type fin. Small portions of the reactor content were sampled through a sintered metal filter with 5 μm mesh at various intervals during the extraction experiments. The calcium content of the filtered solution was determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Hitachi, P-4010).

3.2.3 Confirmation of the technical feasibility of the process

The technical feasibility of the proposed recycling process was examined. By the procedure described above, a 1-hour carbonic acid treatment was carried out on the waste cement sample. After the water evaporated a white powder was obtained and its composition analyzed using X-ray diffraction analysis (Rigaku, Mini Flex) and X-ray fluorescence analysis (JEOL, JSX-3220). The X-ray diffraction pattern of the particles remaining after evaporation of water from the sampled solution was similar to that of calcite. X-ray fluorescence analysis demonstrated that the calcium fraction of the metal content in the remaining particles was larger than 97%. The results show that high purity $CaCO_3$ (calcite) can be obtained from waste cement particles by the extraction procedures used in these experiments.

3.2.4 Maximum calcium utilization ratio from waste cement

Measurements of the maximum conversion rate of calcium were carried out. For this, extraction experiments under excess water conditions and using a sieved sample were conducted. The extraction conditions for each experiment were as follows: (I) p_{CO2} = 0.9 MPa, waste cement / water (C/W) ratio = 0.00143, (II) 3.0 MPa, 0.00286, (III) 3.0 MPa, 0.00286, and a sieved sample of 53 μm was used. The extraction experiments were conducted at a fixed stirring speed (900 rpm) and temperature (323 K). Figure 3.5 demonstrates the results of the experiments.

Figure 3.5. Variations over time of the rate of calcium extraction from the waste cement sample

The calcium extraction rate was defined as: (calcium extraction rate) = (calcium concentration in water [g/g]) ×(C/W ratio [-])×(calcium content ratio of waste cement sample [-])×100 [%]. The calcium extraction rate rapidly increased at the initial stage of extraction and then leveled off after 30 minutes. Maximum extraction rates were not greater than 80%. There are two possible reasons for this. First, the existence of calcium that was physically difficult to extract. This is supported by the experimental result that calcium extraction occurred quickly from small sized waste cement particles, so if the extraction time was longer the extraction rate would increase. Second, the existence of calcium chemically difficult to extract using carbonic acid. The waste cement sample contains some hardly-soluble calcium compounds such as $CaSO_4$, and in such an insoluble form it cannot be extracted by carbonic acid. However, up to about 80% of calcium contained in waste cement can be converted to $CaCO_3$ by the proposed recycling process.

3.2.5 Influence of the extraction temperature on the calcium extraction rate

The extraction temperature has various effects; (I) on the calcium extraction reaction rate, (II) on the saturated solubility of calcium in solution, and (III) on the mass transfer rate at the surface of waste cement particles. Figure 3.6 shows the results of these experiments where the temperature was changed in a range of 291 K to 353 K under conditions of a fixed stirring speed of 500 rpm, p_{CO2} (3.0 MPa) and a C/W ratio (0.033). Figure 3.6 shows the results of the experiments.

Figure 3.6. Influence of extraction temperature on the time course of calcium concentration in the water phase

The doted line in the graph denotes the saturated concentration of Ca^{2+} for each extraction condition calculated from the thermodynamic calculations of the Ca-H_2O-CO_2 system. The temperature effect was complicated; indeed, no clear trend was observed for the initial extraction rate over the temperature range studied (291 K to 353 K). This was caused by the opposing effects of increasing temperature, thermodynamics (lower calcium solubility) and kinetics (higher extraction reaction rate) are involved in the apparent rate of extraction of calcium ions.

3.2.6 The influence of the ratio of waste cement to water on the calcium extraction rate

Figure 3.7 shows the time course for 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).

Figure 3.7. The influence of the initial ratio of waste cement to water on the time course of calcium concentration in the water phase

The doted line in the graph denotes the saturated concentration of Ca^{2+} calculated from the thermodynamic calculations of the Ca-H_2O-CO_2 system. In all cases, calcium concentration increased rapidly during the initial stage of the reaction, for about 10 min, and then leveled off or decreased slightly. The increase in the rate of calcium ions leaching into the solution phase during the initial stage was greater for the case with a larger C/W ratio. The dotted line in figure 3.7 indicates the thermodynamic solubility ($[Ca^{2+}]_{sat}$ = 592 ppm) of calcium ions corresponding to the present experimental conditions. For the calculation of the thermodynamic solubility of $CaCO_3$, we assumed Ca-H_2O-CO_2 system. For conditions with a higher C/W ratio, the solution phase was supersaturated with calcium ions even at a very early stage because of the increase from the source supplying unit quantities of water with Ca^{2+}; this was throughout the extraction experiment, for about 120 min. In the case with the highest C/W ratio (2.9 wt%), supersaturated deviation reached about 3. On the other hand, in the case with the lowest C/W ratio (0.29 wt%), the solution phase never reached supersaturated conditions. The apparent extraction rate described above could be explained by the difference between the extraction of calcium ions from the waste cement and the precipitation of the calcium ions extracted with carbonate ions as calcium carbonate. For cases with larger C/W ratios, where an abundant amount of waste cement is available for the extraction reaction, the extraction rate would be much higher than the precipitation rate, especially during the initial stage of the reaction. This is the reason for the supersaturation observed during the initial stage of the extraction reaction in cases with larger C/W ratios. As the extraction reaction proceeds, the concentration of calcium ions in the aqueous phase would increase, and the amount of waste cement available for the extraction reaction would decrease. Both these conditions would decrease the extraction rate, while the precipitation reaction rate would be increased. This is the reason for the decrease in the apparent extraction reaction rate observed during the later stage of the extraction reaction. The higher C/W ratio increases the rate of calcium ion extraction from the waste cement. However, the portion of calcium extracted from the waste cement in a given extraction time is smaller for conditions with higher C/W ratios. As a result, a larger amount of unreacted waste cement should be recycled, or a larger amount of a waste stream, that is the residues, will be generated in the process. Contrarily, a larger amount of water is necessary for cases with lower C/W ratios. Thus, the required C/W ratio can be determined taking these various trade-offs into consideration.

3.2.7 Influence of CO_2 pressure on the calcium extraction rate

CO_2 pressure has an effect on the saturated solubility of calcium in solution. Figure 3.8 shows the influence of CO_2 pressure (p_{CO2}) on the concentration of calcium ions over time at a fixed stirring rate (900 rpm), temperature (323 K) and initial C/W ratio (0.0029). The doted line in the graph denotes the saturated concentration of Ca^{2+} for each extraction condition calculated from the thermodynamic calculations of the $Ca-H_2O-CO_2$ system.

Figure 3.8. The influence of CO_2 pressure on the time course of calcium concentration in the water phase

The initial extraction rate was found to increase with an increase in 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.

3.2.8 The influence of particle size on the calcium extraction rate

Figure 3.9 shows the influence of the particle size of the waste cement on the concentration of calcium ions over time, at a fixed stirring rate (900 rpm), temperature (323 K), p_{CO2} (3.0 MPa), and initial C/W ratio (0.0029).

Figure 3.9. The influence of particle size on the time course of calcium concentration in the water phase

The initial extraction fraction ratio was found to increase when the average size of waste cement particles decreased. This was because the surface area available for the extraction reaction increases with a reduced particle size.

3.3 $CaCO_3$ precipitation experiments

The precipitation reaction step is of primary importance for producing high-purity calcium carbonate. The detailed experimental studies in this section focus on the effects of operating conditions on the precipitation reaction rates and on the purity of the calcium carbonate produced.

3.3.1 Experimental apparatus

A schematic drawing of the experimental apparatus is shown in figure 3.10.

Figure 3.10. Schematic drawing of the experimental apparatus for the calcium carbonate precipitation experiments

The apparatus consists of two high-pressure stirring tank vessel reactors. The first rector made of HASTELLOY®, a nickel-based alloy, was used for the calcium extraction experiments and had an inner volume of 500 mL; while the precipitation reactor had a 300 mL inner volume, and was made of reinforced glass.

3.3.2 Experimental procedure

All the precipitation reaction experiments were carried out using an aqueous solution obtained from the extraction reaction with given extraction conditions. The solution was transferred to the precipitation reactor after filtration through a sintered metal filter of 5 µm mesh. The precipitation reaction is initiated by reducing CO_2 pressure or increasing temperature. The rate of calcium carbonate precipitation was determined by monitoring the concentration of calcium ions in the solution at various intervals. This was done by a small portion of the solution being sampled with filtration (5 µm mesh), and the calcium concentration determined by ICP-AES (Hitachi, P-4010). After a given period of the precipitation reaction, the remaining reactor contents were taken out and quickly filtered. The chemical composition of the particles remaining on the filter was analyzed by a thermo gravimetric method with a differential thermal analyzer (Shimadzu, DTG-60H).

3.3.3 The influence of the extraction temperature on the $CaCO_3$ precipitation rate

Figure 3.11 shows the influence of temperature on changes in the concentration of dissolved calcium ions, at a fixed stirring rate (500 rpm), CO_2 pressure (0.2 MPa), and amount of seed crystal (0.05 g/200 mL-water). The rate of $CaCO_3$ precipitation increased with an increase in temperature because the solubility of calcium ions in water decreases with an increase in solution temperature, and this increases the precipitation driving force. The precipitation rate was negatively affected by the degree of supersaturation ($[Ca^{2+}]/[Ca^{2+}]_{sat}$). If $[Ca^{2+}]_{sat}$ decreases; if the degree increases then the precipitation rate increases.

Figure 3.11. The influence of the precipitation temperature on the time course of the calcium concentration in the water phase

3.3.4 The influence of CO_2 pressure on the $CaCO_3$ precipitation rate

Figure 3.12 shows the influence of CO_2 pressure on the precipitation rate, at a fixed stirring rate (500 rpm), precipitation temperature (303 K), and amount of seed crystal (0.05 g/200 mL-water). The precipitation rate of $CaCO_3$ decreased with an increase in the pressure of CO_2 due to the increase in the solubility of calcium under high CO_2 pressure conditions, and this increases the precipitation driving force.

Figure 3.12. The influence of CO_2 pressure on the time course of the calcium concentration in the water phase

3.3.5 The influence of the amount of seed crystal on the $CaCO_3$ precipitation rate

Figure 3.13 shows the influence of the amount of $CaCO_3$ seed crystal on the precipitation rate, at a fixed stirring rate (500 rpm), precipitation temperature (303 K), and pressure of CO_2 (0.2 MPa). 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 demonstrating the influence of the operating conditions are consistent with the general characteristic of crystallization from solutions; that is, a lower solubility and a higher surface area enhances the crystallization or precipitation rate of crystals.

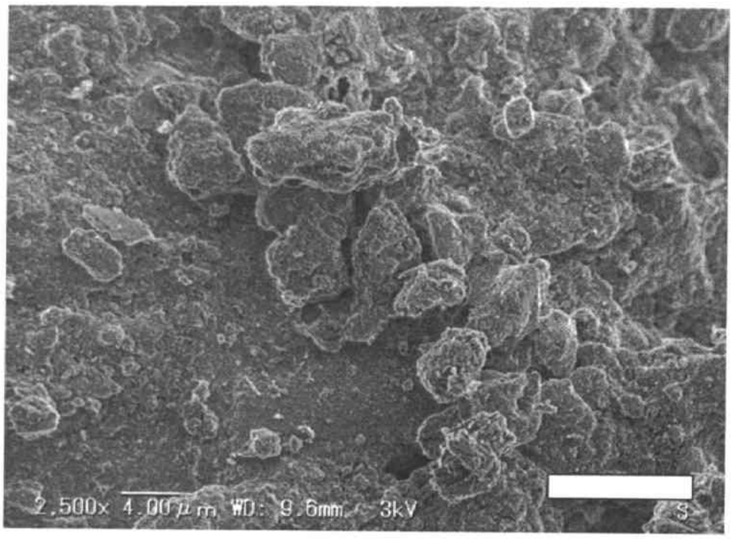
Figure 3.13. The influence of the amount of seed crystal on the time course of the calcium concentration in the water phase

3.4 Purity and particle size distribution of the $CaCO_3$ produced

Thermo-gravimetric analysis indicated that the purity of the precipitated $CaCO_3$ was larger than 98% in the above experiments, and that the intermediate value of the particle size was about 17 μm (the particle size of seed crystal used in this study was about 15 μm). Further, finer (8.4 μm) and purer (99%) $CaCO_3$ particles could be obtained through the precipitation experiment using an adapted N_2 bubbling method.

Reference

Houst Y. F.and Wittmann F. H, 2002, Depth profiles of carbonates fonned during natural carbonation, *Cement and Concrete Reseach,* **32** (12): pp. 1923-1930.



Bar length: 10 µm

Figure 3.1. Surface image of a waste cement particle (SEM)

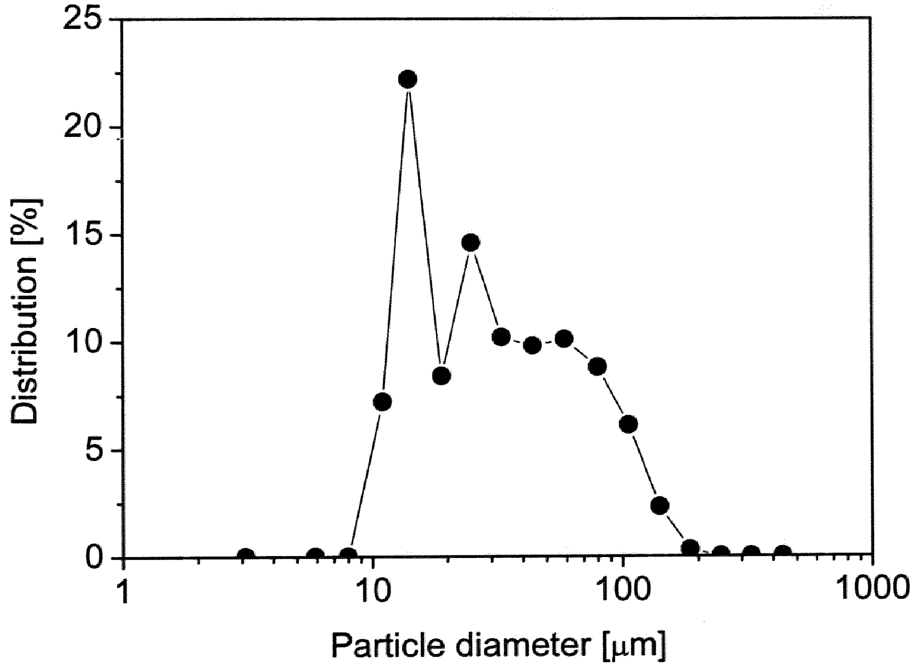


Figure 3.2. Particle size distribution of waste cement particles by light scattering, diameter based on particle surface areas

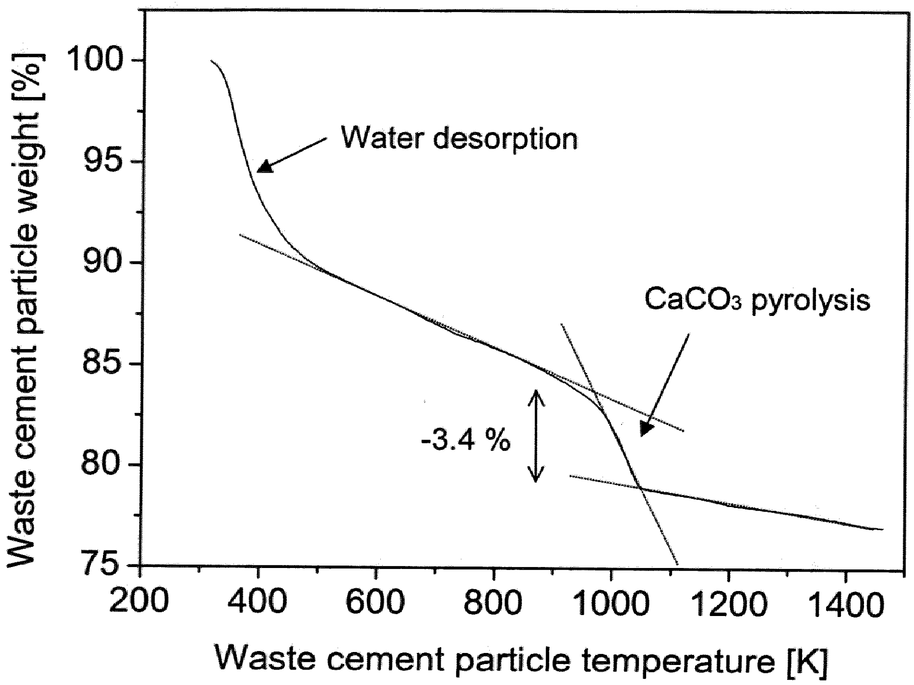


Figure 3.3. Weight variation of waste cement particles on heating

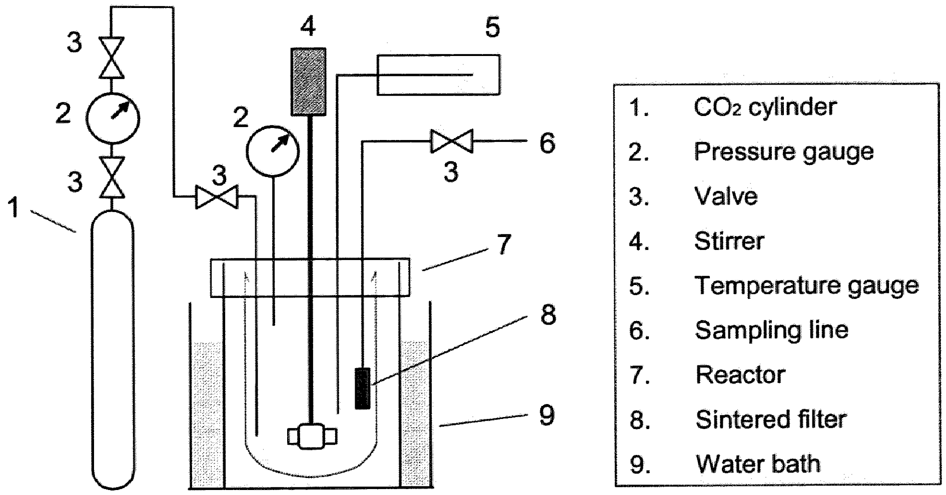


Figure 3.4. Schematic drawing of the experimental apparatus for the calcium extraction experiments

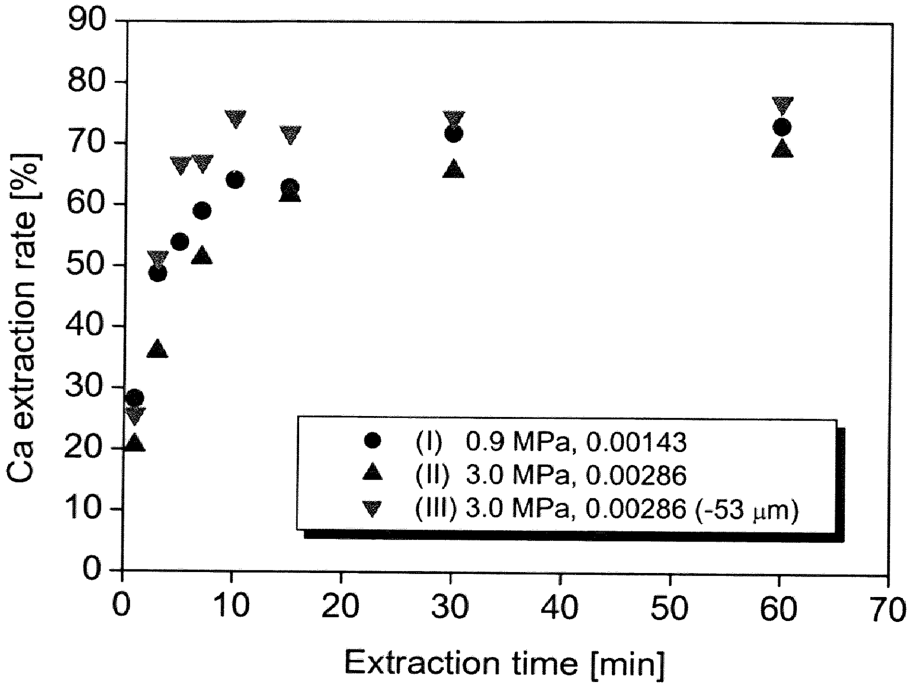


Figure 3.5. Variations over time of the rate of calcium extraction from the waste cement sample

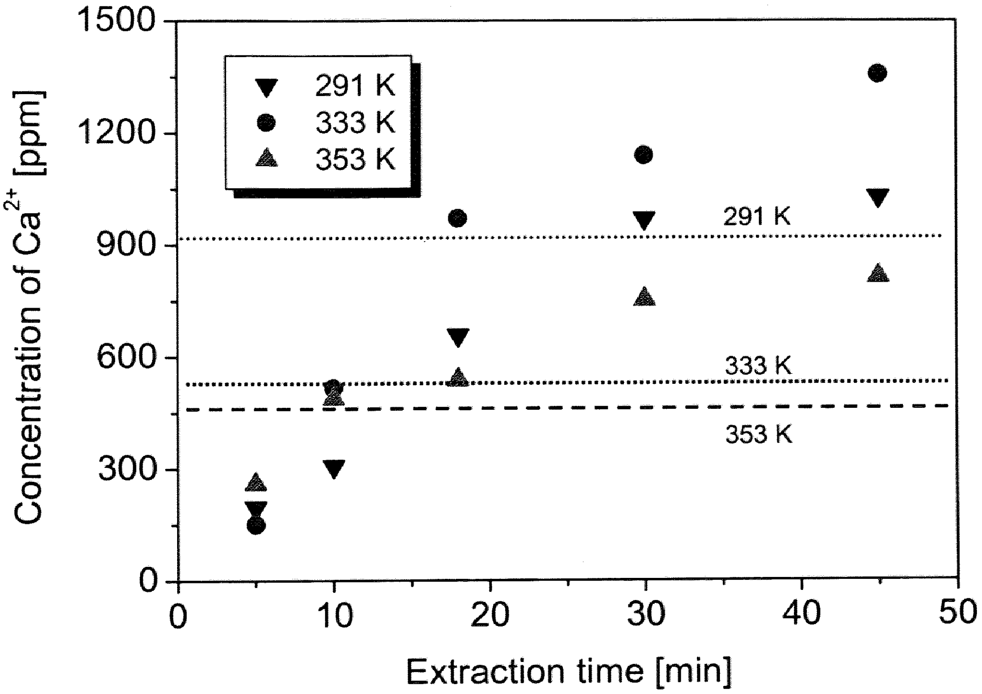


Figure 3.6. Influence of extraction temperature on the time course of calcium concentration in the water phase. The doted line denotes the saturated concentration of Ca^{2+} for each conditions calculated from thermodynamic calculation of the Ca-H_2O-CO_2 system.

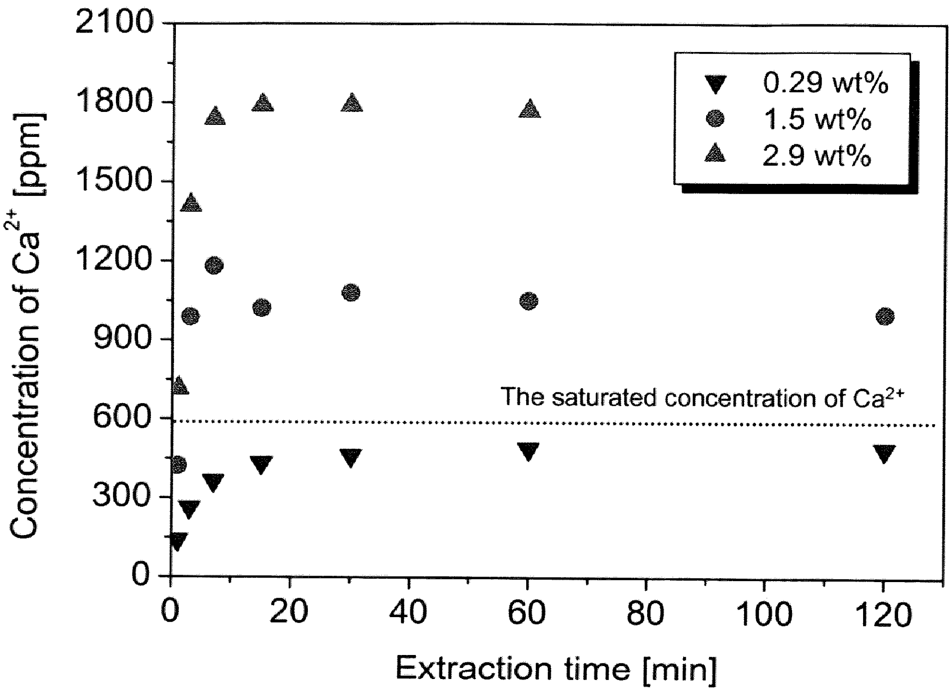


Figure 3.7. The influence of the initial ratio of waste cement to water on the time course of calcium concentration in the water phase. The doted line denotes the saturated concentration of Ca^{2+} calculated from thermodynamic calculation of the Ca-H_2O-CO_2 system.

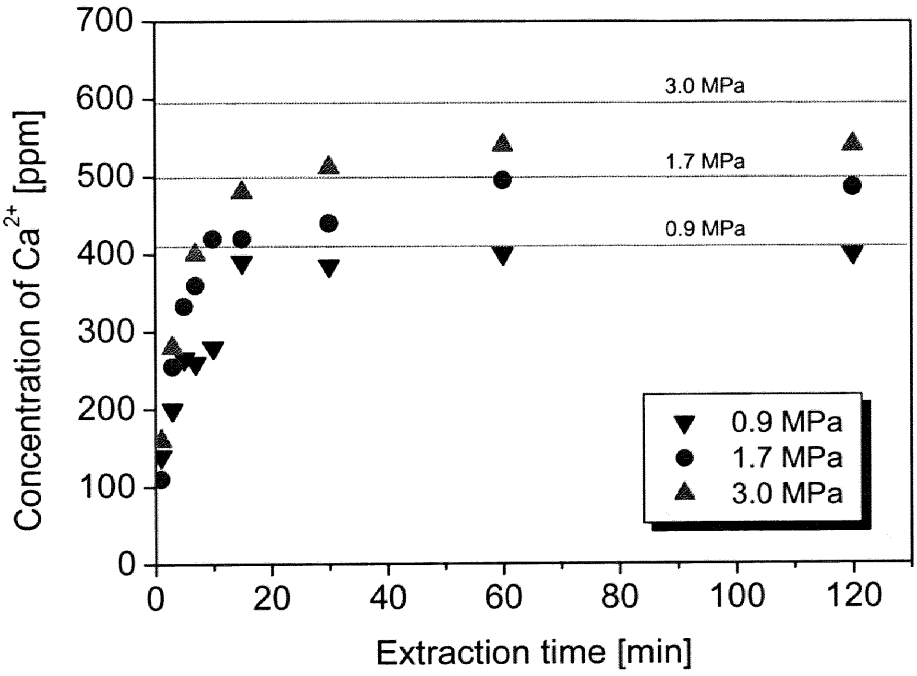


Figure 3.8. The influence of CO_2 pressure on the time course of calcium concentration in the water phase. The doted line in the graph denotes the saturated concentration of Ca^{2+} for each extraction condition calculated from thermodynamic calculation of the Ca-H_2O-CO_2 system.

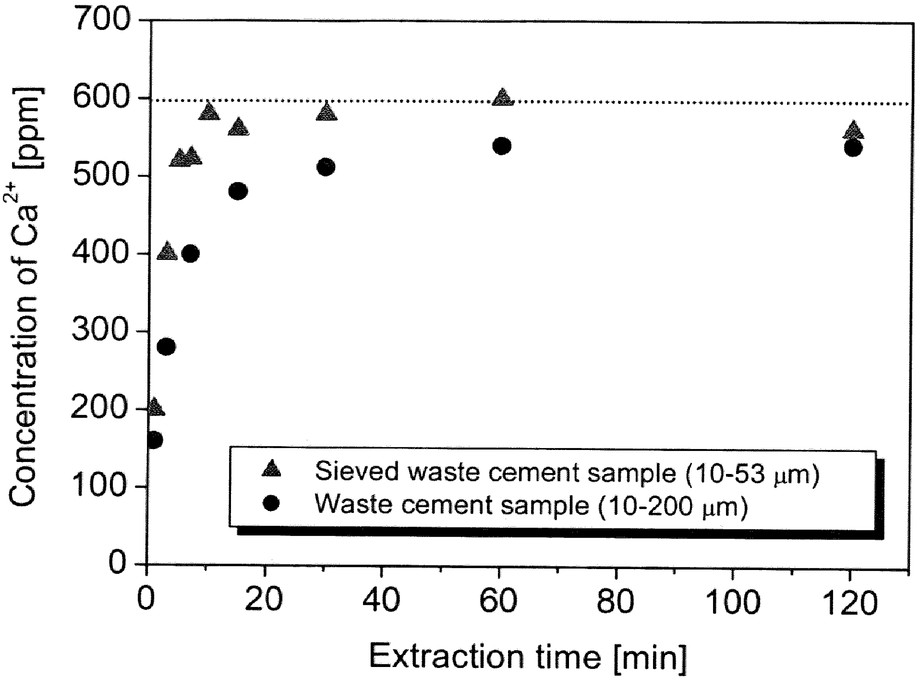


Figure 3.9. The influence of particle size on the time course of calcium concentration in the water phase. The doted line in the graph denotes the saturated concentration of Ca^{2+} calculated from thermodynamic calculation of the Ca-H_2O-CO_2 system.

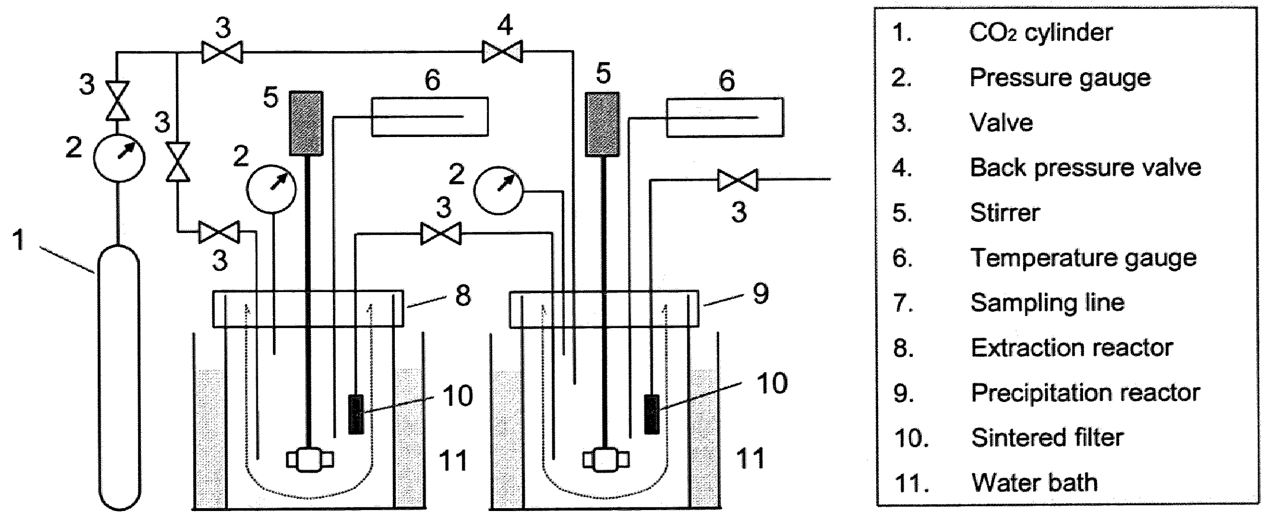


Figure 3.10. Schematic drawing of the experimental apparatus for the calcium carbonate precipitation experiments

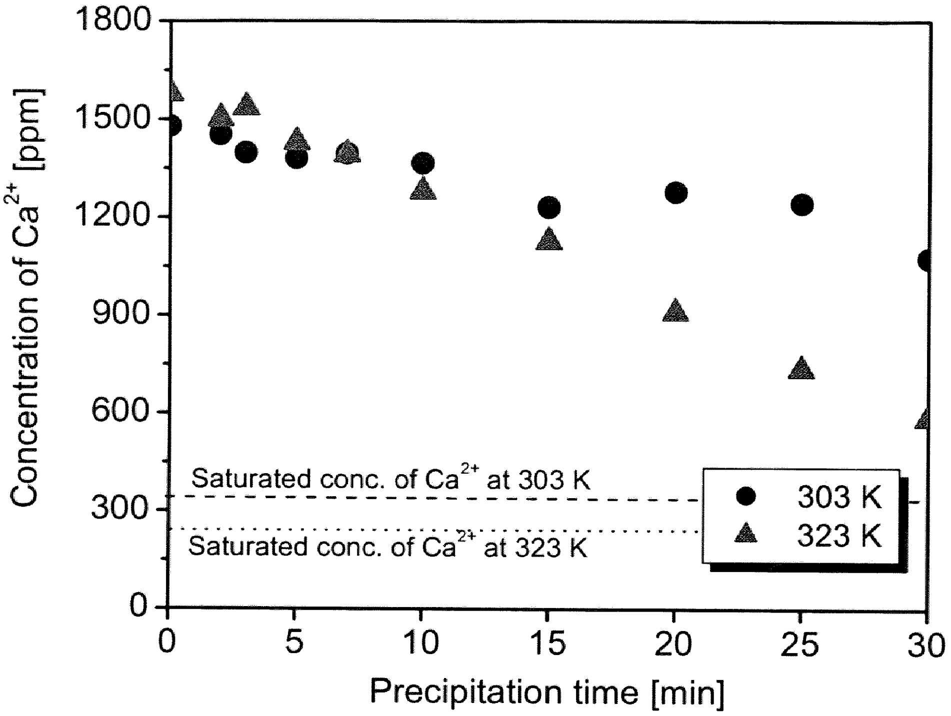


Figure 3.11. The influence of the precipitation temperature on the time course of the calcium concentration in the water phase

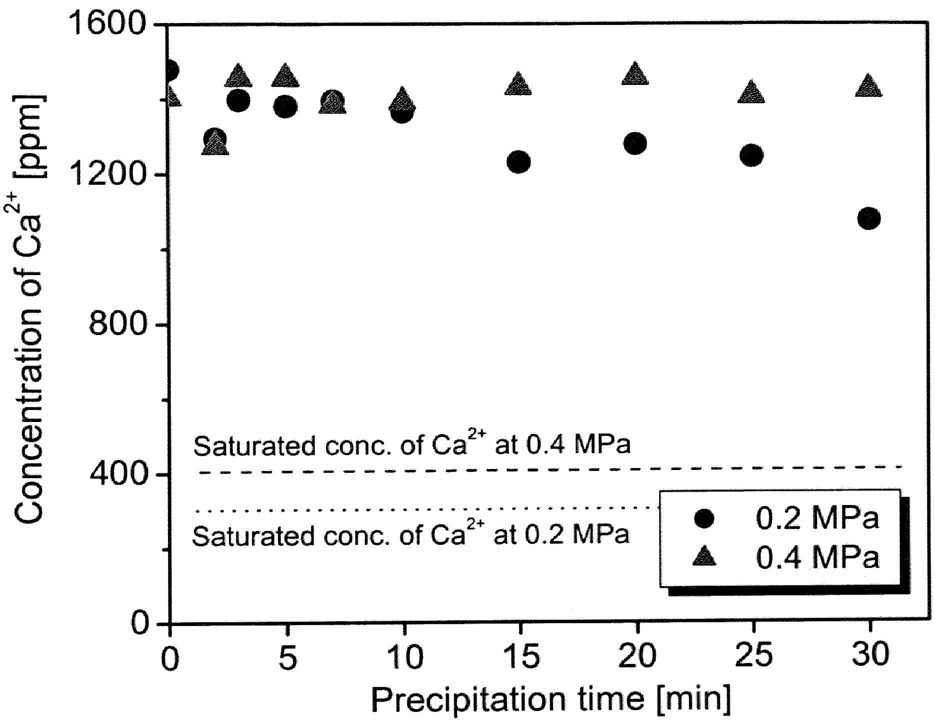


Figure 3.12. The influence of CO_2 pressure on the time course of the calcium concentration in the water phase

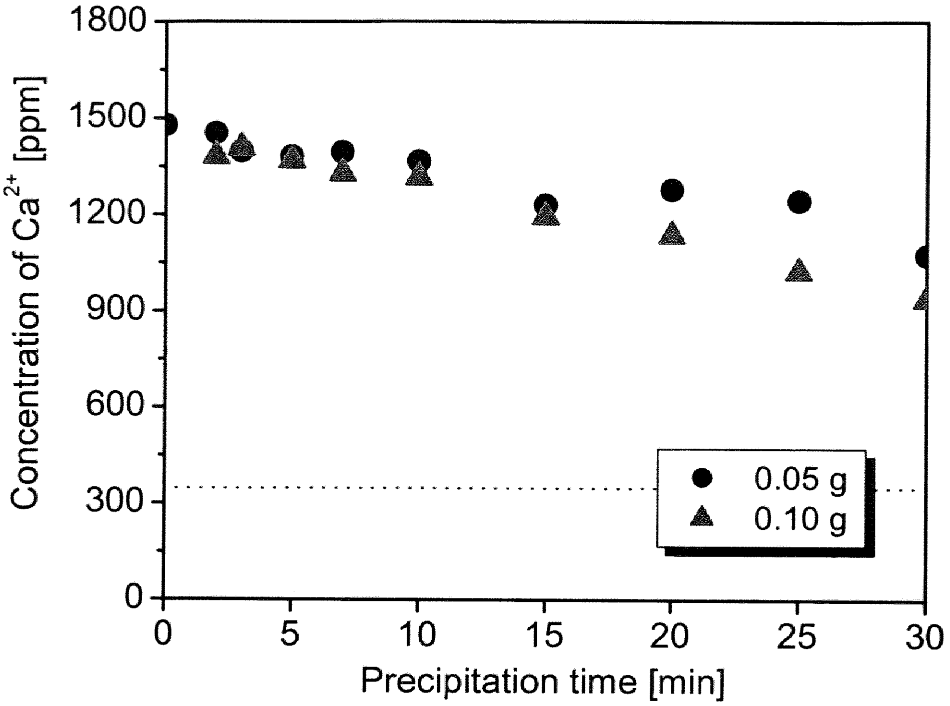


Figure 3.13. The influence of the amount of seed crystal on the time course of the calcium concentration in the water phase

Table 3.1. Light scattering illustration of particle size distribution of the waste cement sample

Average diameter (μm, volume base)	Volume fraction (%)	Surface area fraction (%)	Number fraction (%)
438	0.0	0.0	0.0
327	0.0	0.0	0.0
247	0.0	0.0	0.0
186	1.3	0.3	0.0
141	8.1	2.3	0.0
106	16	6.1	0.2
80	18	8.8	0.6
59	15	10	1.2
44	11	9.8	2.0
33	8.5	10	3.8
25	9.0	15	9.9
19	3.9	8.4	10
14	7.8	22	46
11	1.9	7.2	26
8	0.0	0.0	0.0
6	0.0	0.0	0.0
3	0.0	0.0	0.0

Table 3.2. Elemental content of the waste cement sample

Element	Ca	Si	Fe	Al	S	K	Mn	Zn	Mg	Na	Total
Mass content [wt-%]	27.3	6.46	4.32	1.12	0.52	0.21	0.18	0.06	0.05	-	40.2%

Table 3.3. Estimated chemical composition of the waste cement sample

Element	CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	K_2O	MnO	ZnO	MgO	Total
Mass content [wt-%]	38.2	13.8	12.4	4.2	1.3	0.5	0.2	0.1	0.1	70.8%

4. Empirical formulation of treatment rates

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References

4. Empirical formulation of treatment rates

4.1 Empirical formulation of calcium extraction treatment rate from waste cement particle

In this section, empirical formulations of calcium extraction treatment rates from waste cement is discussed. For this, a simple proportional expression was adapted, and just the calcium extraction reaction rate in the initial stage of extraction is formulated. However, even a more complicated empirical formula based on kinetic theory for mass transfer at the particle surface is still unable to express the extraction behavior in the late stage of extraction.

4.1.1 Extraction temperature dependency

The extraction temperature is considered to influence three parameters: (I) the extraction reaction rate of calcium, (II) saturated calcium solubility, and (III) the mass transfer rate at the particle surface. In this section, these three parameters are considered theoretically.

(I) The extraction reaction rate of calcium

The calcium extraction reaction rate is considered to depend on an Arrhenius type temperature dependency given by

$$k = A\exp\left(-Ea/RT\right) \qquad \text{(Eq. 4.1)}$$

where k is a velocity coefficient, Ea is the activated energy of reaction, A is a frequency factor, R is a gas constant, and T is the reaction temperature. The reaction rate exponentially increases with an increase in temperature.

(II) Saturated calcium solubility

The saturated solubility of calcium can be estimated by thermodynamic consideration of the Ca-H_2O-CO_2 system. Figure 4.1 indicates the saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature (see Appendix II).

Figure 4.1. The saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature (CO_2 pressure dependency)

With an increase in temperature, the saturated solubility of the calcium ion concentration decreases. Calcium extraction is driven by the calcium ion concentration difference between the waste cement surface and the bulk of solution; so a calcium ion solubility decrease causes an extraction rate decrease.

(III) Mass transfer rate at the particle surface

The mass transfer rate at the particle surface is accelerated by an increase in temperature. This is due to the increase of the diffusion coefficient of calcium in water with a temperature increase. A variety of empirical formulas for temperature dependency of the ion diffusion coefficient in water phase have been proposed; for example, in several empirical formulas the diffusion coefficient is proportional to the first order transition of temperature.

The appropriate temperature for calcium extraction is determined from the above factors. The effects of temperature on calcium extraction from concrete waste are shown in table 4.1.

Table 4.1. Effects of temperature on calcium extraction from concrete waste

As expected from table 4.1, the temperature dependency observed was complex (refer to section 3.2.4, and figure 3.6). Because waste heat is often available near intensive CO_2 emission sources such as thermal power, cement and steel plants, the process temperature can be obtained relatively easily. Thus, the temperature dependency of calcium extraction rate was not formulated, but was fixed at 323 K, while other dependencies were considered.

4.1.2 Particle size dependency

The particle sizes in waste cement influence on (I) the volume based specific surface area of the particles, and (II) the diffusion behavior of calcium ions at the particle surface in a stirring vessel. In theory, the calcium extraction rate is proportional to the first order of the surface area, thus it is proportional to the inverse of the radius if the amount of waste cement is fixed. The experimental results for samples with different particle sizes are showed in figure 4.2.

Figure 4.2. The influence of particle size on the time course of the calcium concentration in the water phase. (Figure 3.9)

The initial extraction fraction ratio was found to increase when the average size of the waste cement particles decreased. This is because the surface area available for the extraction reaction increases as particle size reduces. For each sample with a different particle size, the total particle surface area was estimated from particle size measurements. Further, the initial (up to 10 min) extraction rates of calcium ions from waste cement particles were calculated from these experimental results. From this the following empirical formula for the dependency on the surface area of waste cement was obtained.

$$\text{(Initial extraction rate of calcium)} = \alpha \times \text{(total surface area of waste cement)}^{1.0} \qquad \text{(Eq. 4.2)}$$

where α is a proportional constant.

4.1.3 CO_2 pressure dependency

The rate of increase in the calcium concentration during the initial stage of the reaction was found to increase with an increase in CO_2 pressure (refer to section 3.2.6). The increase in the initial extraction rate with increasing CO_2 pressure could be attributed to the increase in the solubility of calcium ions. With an increase in solubility, the driving force of the extraction reaction would increase and result in the increased extraction rate. Figure 4.3 shows the initial (until 10 min) extraction reaction rate change as a function of the partial pressure of CO_2, based on figure 3.10.

Figure 4.3. The calcium extraction rate during the initial stage of the reaction (first 10 min for all runs) as a function of the partial pressure of CO_2.

The initial extraction rates were approximately proportional to about a quarter power of the partial pressure of CO_2. Thus, the initial extraction rates were expressed by following equation under a fixed stirring speed (900 rpm), extraction temperature (323 K), and C/W ratio (0.0029):

$$(\text{Initial extraction rate of calcium}) = \beta \times (CO_2\ \text{pressure})^{0.25} \qquad \text{(Eq. 4.3)}$$

where β is a proportional constant.

4.1.4 The waste cement to water ratio (C/W ratio) dependency

Figure 4.4 shows the initial (until 10 min) extraction reaction rate change as a function of the ratio of waste cement to water based on figure 3.9.

Figure 4.4. The calcium extraction rate during the initial stage of the reaction (first 10 min for all runs) as a function of the ratio of waste cement to water

The initial extraction rates were approximately proportional to about a quarter power of the partial pressure of CO_2. Thus, the initial extraction rates were expressed by the following equation under a fixed stirring speed (900 rpm), extraction temperature (323 K), and CO_2 pressure (3.0 MPa):

$$\text{(Initial extraction rate of calcium)} = \gamma \times \text{(ratio of waste cement to water)}^{0.74}$$

(Eq. 4.4)

where γ is a proportional constant.

4.1.5 Calcium extraction rate formulation

From the above discussion, and Eq. 4.2, 4.3, 4.4, the initial extraction ratio of calcium from waste cement particle is given by

$$\begin{aligned}\text{(Initial extraction rate of calcium)} &= \delta \times \text{(total surface area of waste cement)}^{1.0}\\ &\times (CO_2\ \text{pressure})^{0.25}\\ &\times \text{(ratio of waste cement to water)}^{0.74}\end{aligned}$$

(Eq. 4.5)

where δ is a proportional constant. It is noted that this relational equation can be used under the extraction condition of stirring speed (900 rpm), extraction temperature (323 K), C/W ratio (0.0029-0.029), and CO_2 pressure (0.9-3.0 MPa).

4.2 Empirical formulation of calcium carbonate precipitation

4.2.1 Calcium carbonate precipitation theory

In the Ca-H_2O-CO_2 system, the precipitation rate of $CaCO_3$ is given by the following equation (T. F. Kazmierczak et al, 1982).

$$-\frac{d[Ca^{2+}]}{dt} = ks\,(\sqrt{[Ca^{2+}][CO_3{}^{2-}]} - \sqrt{K_{sp}})^2 \qquad \text{(Eq. 4.6)}$$

where k is a velocity constant [m^4/mol/s], s is the concentration of the precipitation area [m^2/m^3], K_{sp} represents the solubility product constants for $CaCO_3$ [mol^2/m^6]:

$$K_{sp} = [Ca^{2+}]_{sat}[CO_3^{\ 2-}]_{sat} \qquad \text{(Eq. 4.7)}$$

By assuming an equality of the degree of supersaturation of calcium ions and carbonate ion in Eq. 4.6,

$$-\frac{d[Ca^{2+}]}{dt} = ks \cdot K_{sp}\left(\frac{[Ca^{2+}]}{[Ca^{2+}]_{sat}} - 1\right)^2 \qquad \text{(Eq. 4.8)}$$

Eq. 4.8 is obtained. Consequently, increasing *k*, *s*, and the degree of supersaturation of calcium ions can accelerate the $CaCO_3$precipitation rate. (I) Precipitation temperature, (II) CO_2 pressure, (III) the amount of seed crystal, and (IV) the stirring rate are considered as the experimental (or operational) parameters that can vary the above, initially stated, parameters.

(I) Precipitation temperature

The saturated solubility of $CaCO_3$ strongly depends on the temperature of the solution (refer to figure 4.1). A temperature increase causes an increase in the degree of supersaturation of calcium ions because of the decrease in the saturated solubility. Further, generally the velocity coefficient increases with the temperature increase (refer to Eq. 4.1). Thus, precipitation reaction itself quickly occurs in high temperature.

(II) CO_2 pressure

A decrease in CO_2 pressure causes the saturated solubility of $CaCO_3$ (refer to figure 4.1); thus, accelerating the precipitation rate.

(III) Amount of seed crystal

The surface of $CaCO_3$ for precipitation increases with an increase of the amount of seed crystal; therefore, the precipitation rate of $CaCO_3$ is derived from the seed crystal fed to the precipitation reactor.

(IV) Stirring rate

An increase of the stirring rate in the $CaCO_3$ precipitation reactor provides for a decrease in the thickness of the diffusion layer at the surfaces of seed crystal particles, and so increases the $CaCO_3$precipitation rate.

Influences of above factors are summarized in table 4.2.

Table 4.2. Effects of the precipitation conditions on calcium carbonate precipitation

4.2.2 Precipitation velocity constant

k in Eq. 4.8 is a velocity coefficient, and strongly depends on temperature; in this study an Arrhenius type temperature dependency was assumed.

$$k = A\exp(-Ea/RT) \qquad \text{(Eq. 4.1)}$$

where *E*a is the activated energy of the reaction, *A* is a frequency factor, *R* is a gas constant, and *T* is the reaction temperature. In this section, the determination of *E*a of the $CaCO_3$ precipitation reaction was done based on the experimental results of the precipitation.

Figure 4.5 and 4.6 illustrates a comparison between the experimental results and the model output based on Eq. 4.8 at 303.15 K and 323.15 K for various values of velocity coefficient *k*.

Figure 4.5. Comparison between the experimental results and the model output for various values of velocity coefficient *k* at 303.15 K

Figure 4.6. Comparison between the experimental results and the model output for various values of velocity coefficient *k* at 323.15 K

From the comparison, coefficient velocity *k* is estimated to be 0.152 mol m^4/s at 303.15 K, and 0.321 mol m^4/s at 323.15 K, respectively. Consequently, for $CaCO_3$ precipitation, Eq. 4.1 can now be given as follows.

$$k = (2.63\times10^{4})\cdot\exp(-\frac{3.04\times10^{4}}{8.314\cdot T})\ \ [\text{mol m}^4/\text{s}] \qquad \text{(Eq. 4.9)}$$

4.2.3 The precipitation surface of calcium carbonate

In this study, the surface area that can contribute to $CaCO_3$ precipitation was assumed to be 0.3 m^2/g-$CaCO_3$. Total surface area variation with precipitation time was also considered.

4.2.4 The saturated concentration of calcium carbonate

The solubility product constant of $CaCO_3$ depends on temperature, and here is assumed to be expressed in the following equation (Michael M. Reddy and George H. Nancollas, 1971).

$$\log K_{sp} = \frac{449.74}{T} - 9.942 \qquad \text{(Eq. 4.10)}$$

4.2.5 Conclusion

Based on the above considerations for the formulation of the calcium carbonate precipitation rate, a comparison between the experimental results and the model output for other precipitation conditions was conducted. Figure 4.7 and 4.8 illustrate the results of the comparison.

Figure 4.7. Comparison between the experimental results and the model output (I)

Figure 4.8. Comparison between the experimental results and the model output (II)

Good accordance is observed in both cases. Thus, it is considered that the empirical formula obtained here is useful for evaluations of $CaCO_3$ precipitation rates.

4.3 Conclusion of empirical formulation

Even under the limited operating conditions, the calcium extraction rate from waste cement particles could be formulated. A precise formula for the $CaCO_3$ precipitation rate under various conditions was obtained. In the following chapters, based on these results, an evaluation of the process will be conducted.

References

T. F. Kazmierczak et al., 1982, Crystal Growth of Calcium Carbonate. A Controlled Composition Kinetic Study, *The Journal of Physical Chemistry*, 86(1), pp. 103-107.

Michael M. Reddy and George H. Nancollas, 1971, The Cristallization of Calcium Carbonate I. Isotopic Exchange and Kinetics, *Journal of Colloid Interface and Science*, 36(2), pp. 166-172.

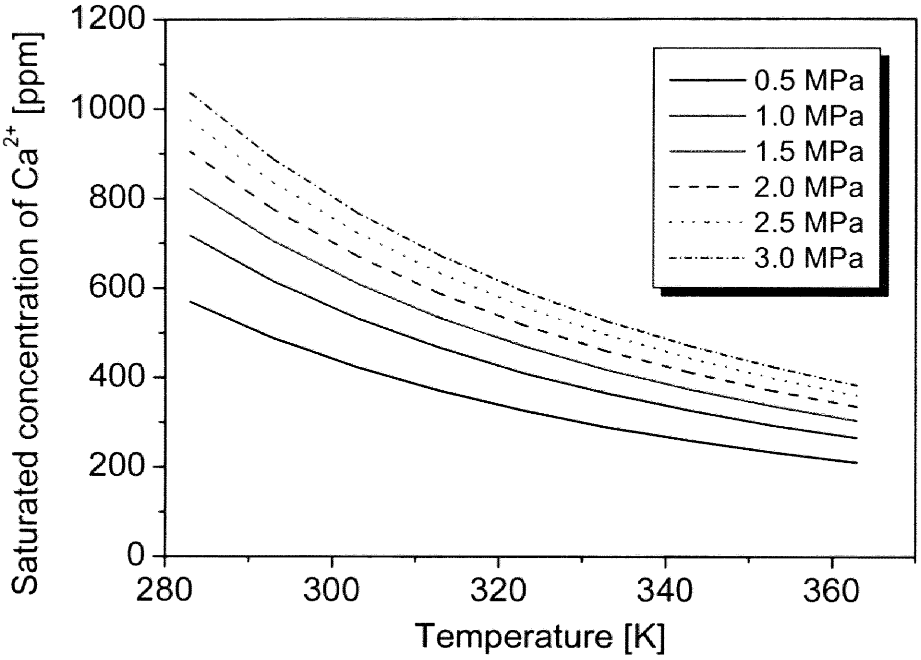

Figure 4.1. The saturated Ca^{2+} concentration in the Ca-H_2O-CO_2 system as a function of temperature (CO_2 pressure dependency) (figure II.4)

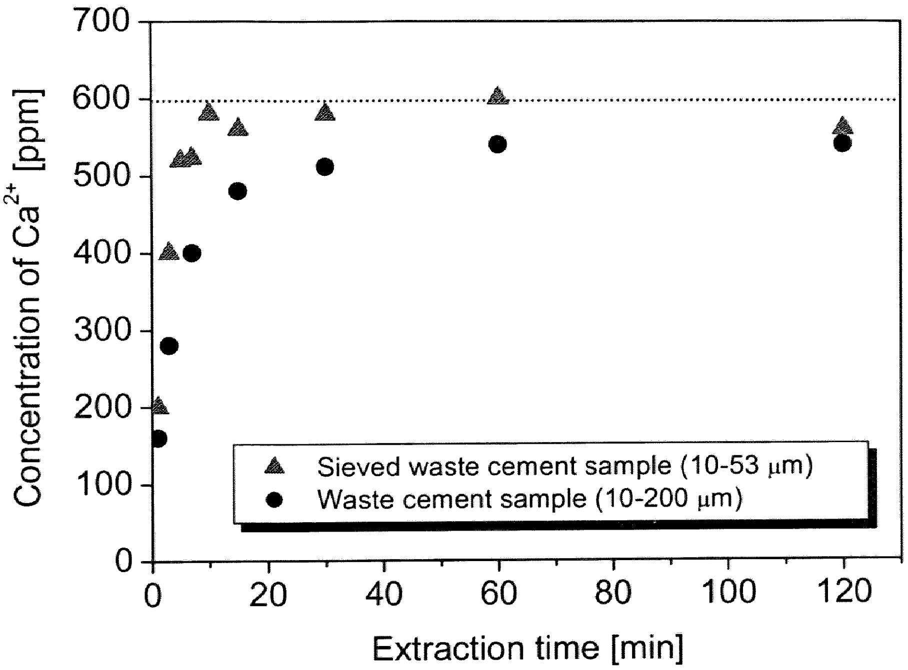

Figure 4.2. The influence of particle size on the time course of the calcium concentration in the water phase (Figure 3.9). The doted line in the graph denotes the saturated concentration of Ca^{2+} calculated from thermodynamic calculation of the Ca-H_2O-CO_2 system.

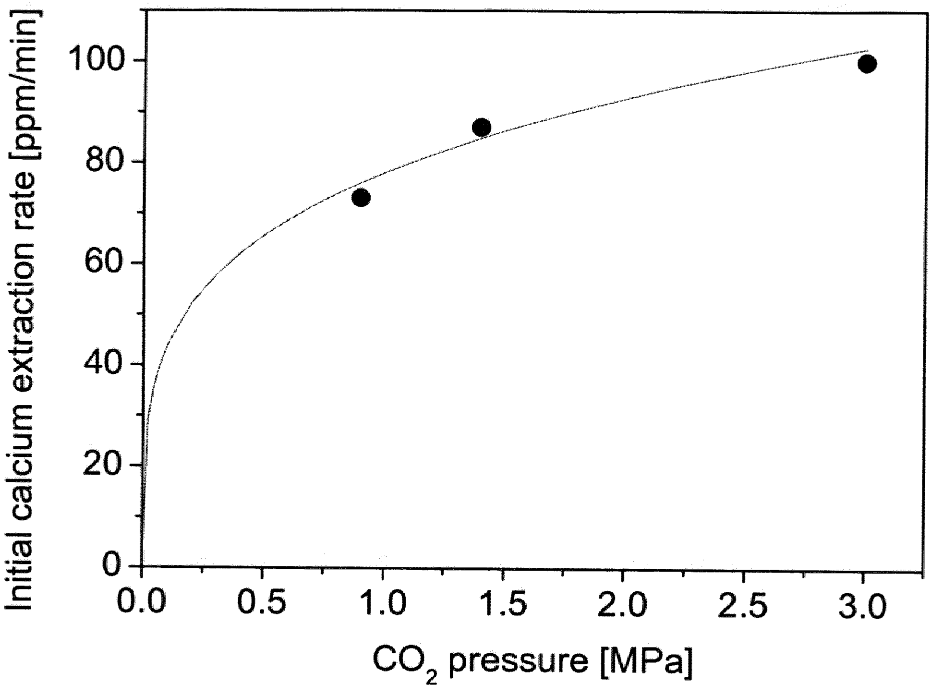

Figure 4.3. The calcium extraction rate during the initial stage of the reaction (first 10 min for all runs) as a function of the partial pressure of CO_2

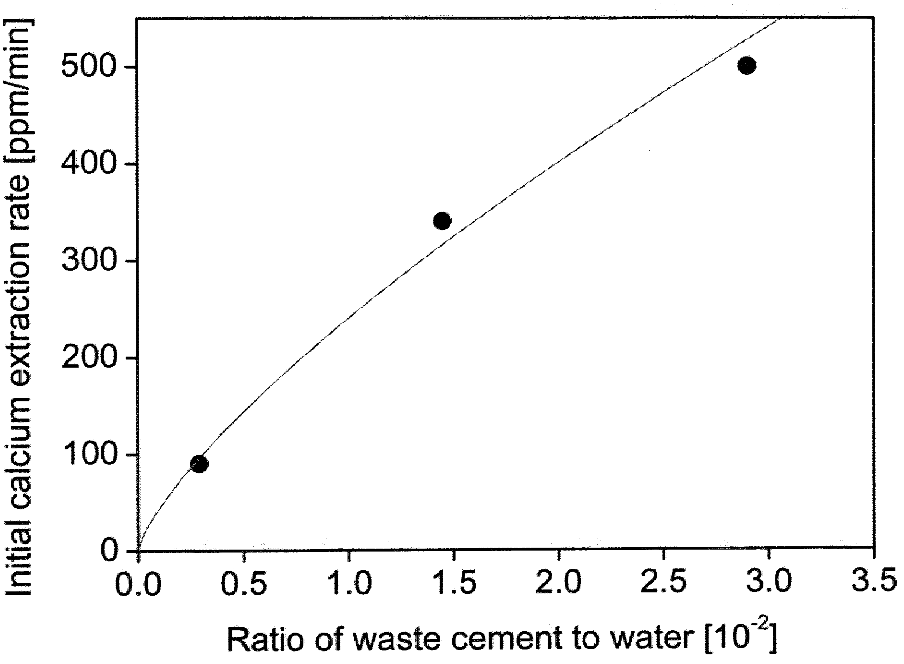

Figure 4.4. The calcium extraction rate during the initial stage of the reaction (until 10 min for all runs) as a function of the ratio of waste cement to water

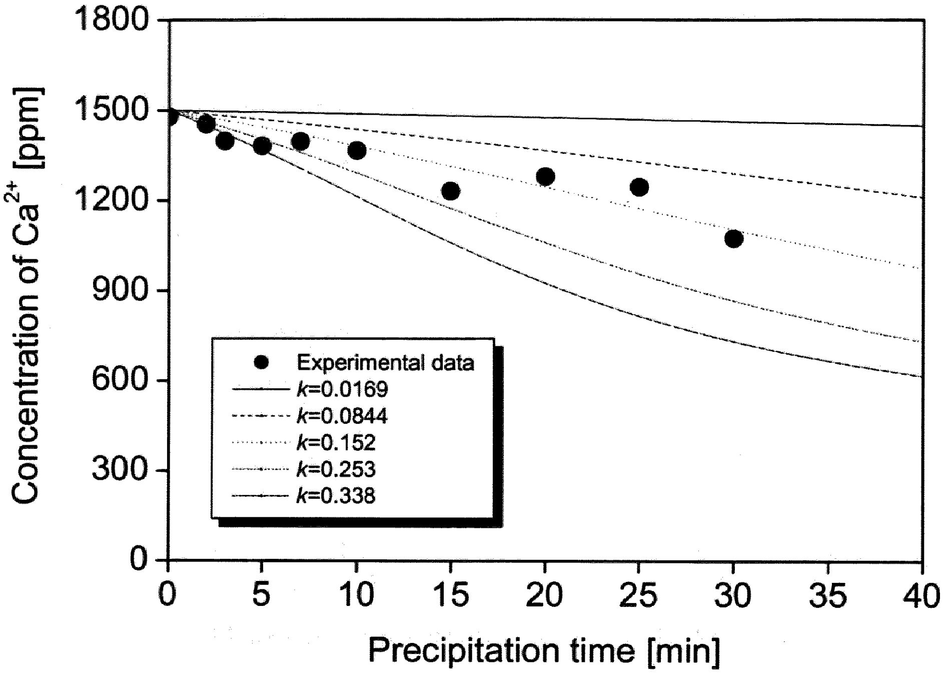

Figure 4.5. Comparison between the experimental results and the model output for various values of velocity coefficient k at 303.15 K

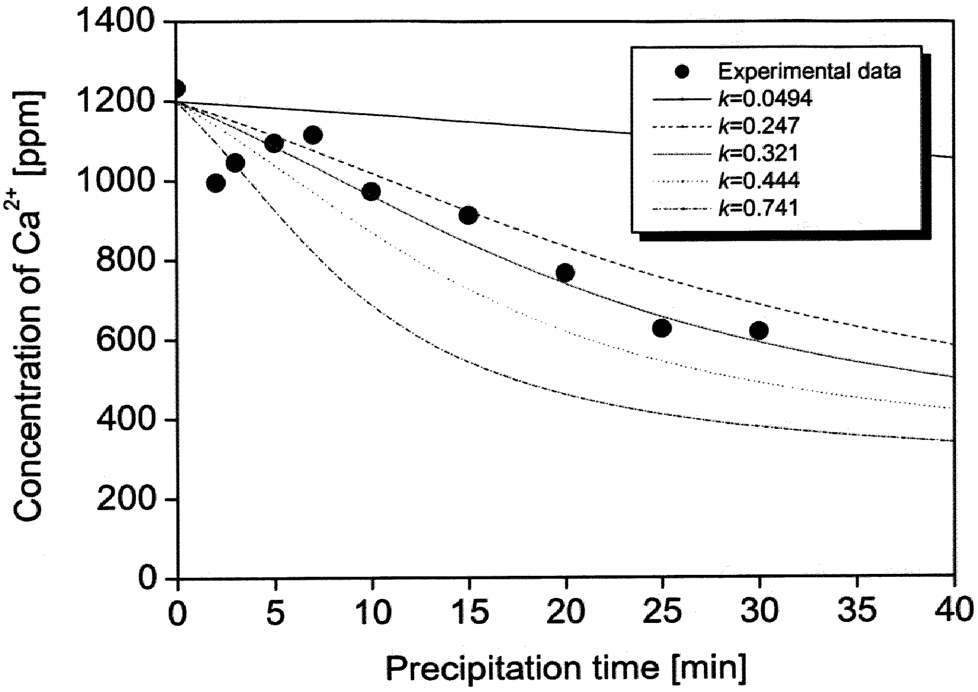

Figure 4.6. Comparison between the experimental results and the model output for various values of velocity coefficient k at 323.15 K

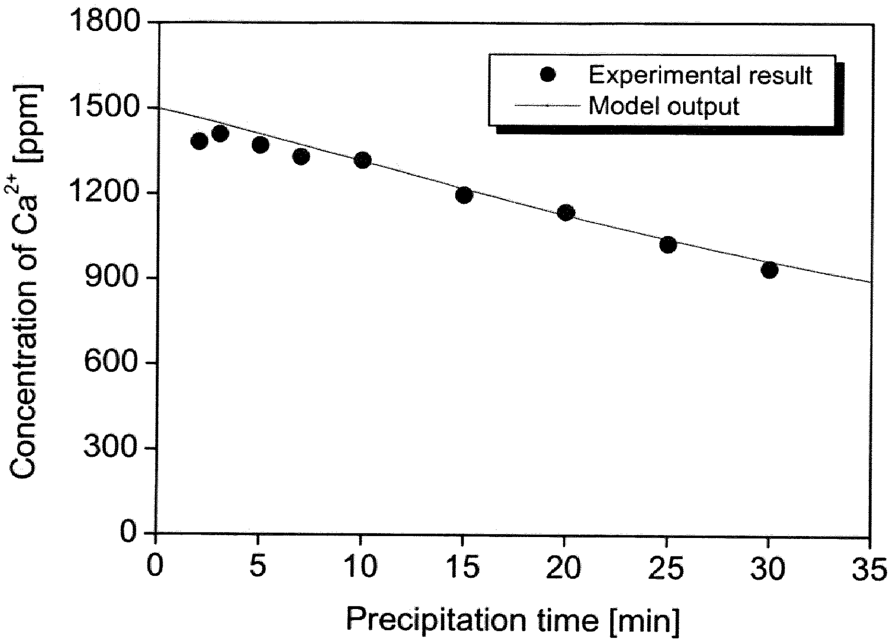

Figure 4.7. Comparison between the experimental results and the model output (I)

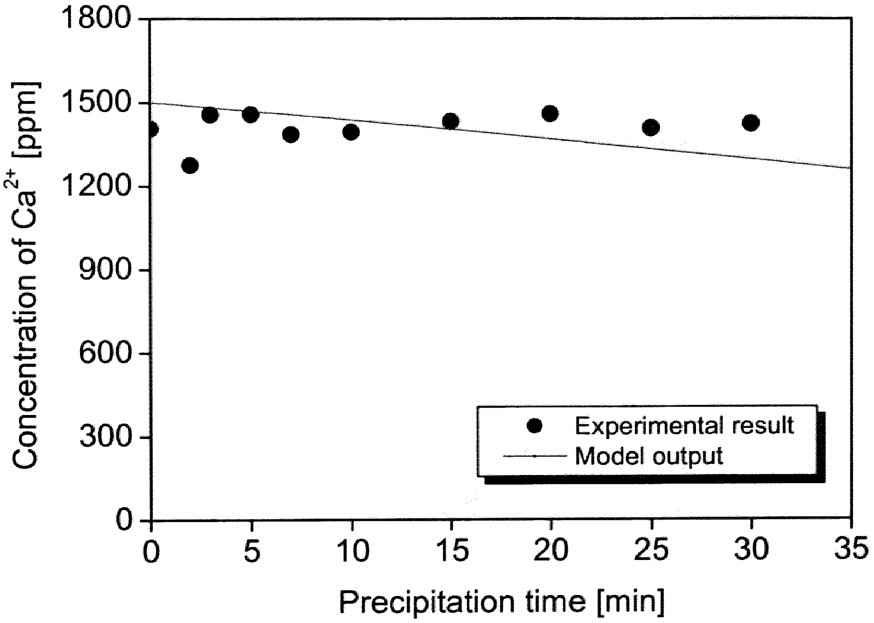

Figure 4.8. Comparison between the experimental results and the model output (II)

Table 4.1. Effects of temperature on calcium extraction from concrete waste

Temperature	up ↗	down ↘
Extraction reaction rate	↗	↘
Saturated calcium solubility	↘	↗
Mass transfer rate at the particle surface	↗	↘

Table 4.2. Effects of the precipitation conditions on calcium carbonate precipitation

	Precipitation temperature	CO_2 Pressure	Seed crystal amount	Stirring rate
	↗	↗	↗	↗
Velocity constant	↗	-	-	-
Precipitation surface area	-	-	↗	↗
Saturated calcium solubility	↘	↗	-	-
Mass transfer rate	↗	-	-	↗

5. Design of the proposed recycling plant

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5. Design of the proposed recycling plant

5.1 Composition of the recycling plant

In this study, the following nine facilities were considered necessary to constitute the proposed concrete waste recycling plant.

Calcium extraction reaction related facility:
  (I) Calcium extraction reactor
Calcium carbonate ($CaCO_3$) precipitation reaction related facility:
  (II) $CaCO_3$ precipitation reactor
Storage facilities:
  (III) Silo for waste cement powder, and
  (IV) Silo for the $CaCO_3$ produced
Other facilities:
  (V) Carbon dioxide (CO_2) capturing facility, (VI) CO_2 compressor,
  (VII) Air compressor, (VIII) Pulverizer, and
  (IX) Waste water treatment facility

Storage facilities were not prepared for materials that can tolerate storage as an outdoor pile, such as extraction residues. A typical example of a recycling plant is illustrated in figure 5.1.

Figure 5.1. An example of the composition of the proposed concrete waste recycling plant

Input materials for the recycling plant are only water, CO_2, and waste cement powder. Output materials are the $CaCO_3$ produced, wastewater, extraction residue, and CO_2. Water is recycled for use in the treatment, and for this is partly treated at the waste water treatment facility. CO_2 used in the plant is captured by a chemical capturing method using alkanolamine from the flue gas from a CO_2 intensive emission source. The

CO_2 fed at high pressure is partly converted to $CaCO_3$, and any unreacted CO_2 is recovered at a lower pressure, and recirculated for reuse, or is vented to the atmosphere. Waste cement is treated with carbonic acid for calcium extraction in the extraction reactor, and extracted residue is generated. The main component of the residue is considered to be silica dioxide, which can be sold as recycle sand. Treated wastewater is released to the environment, and an equal amount of water is fed into the plant. The $CaCO_3$ produced is sold in the marketplace.

5.2 Determination of the specifications of each facility

In this section, methods for estimations of scale, capital costs, and the power consumption for each facility are summarized. For the capital cost estimation, scaling-up was undertaken by a power method. The base value of the capital cost for each facility was obtained from an interview with a Japanese company involved in the field. Power consumption was estimated assuming that power consumption is proportional to throughput; the base value was obtained also obtained from an interview with a Japanese company involved in the field.

5.2.1 Calcium extraction reactor

(Scale) A geometrically shaped reactor similar to the experimental apparatus was assumed. The reactor volume required was determined from the throughput of waste cement, the retention time in the extraction reactor, and the extraction reaction rate. For this calculation, the empirical formula presented in chapter 4 was used.

(Capital cost) The capital cost for the extraction reactor was estimated based on the material cost for constructing the reactor. The reactor material is stainless steel, and the amount needed was calculated using the size and the minimum wall thickness assigned by the Japanese Industrial Standards (JIS) for high-pressure vessels. The required thickness is given by

$$t[mm] = \frac{P[kgf/cm^2]\cdot D[mm]}{200\sigma[kgf/cm^2]\cdot 0.25 - 1.2P[kfg/cm^2]} \qquad \text{(Eq. 5.1)}$$

where t is the minimum required thickness for the reactor, P is the maximum design pressure of the reactor, σ is the extensional strength of the reactor substance, and D is the diameter of the reactor. The material cost for the reactor vessel was estimated from the costs of the required substances and the volume calculated from the reactor surface area and thickness. The capital cost for the extraction reactor was assumed to be five times the material cost.

(Power consumption) The power required for stirring, the main area for energy consumption in the extraction process, was estimated by the following scaling-up scheme; the stirring power consumption per unit volume of the scaled-up reactor was equalized to that for the extraction reactor used in the experimental studies. The stirring power for the experimental reactor was estimated based on Nagata's equation (Society of Chemical Engineers, 1999). Energy consumption for stirring is given by

$$W = N_p \rho n^3 d^5 \qquad \text{(Eq. 5.2)}$$

where W [W] is the energy consumption from stirring, Np [-] is power number, ρ [kg/m^3] is the density of the fluid, n [rps] is the stirring rate per second, , d [m] is the diameter of the paddle, and so in Nagata's equation are described as follows;

$$N_p = \frac{A}{\mathrm{Re}} + B\left(\frac{1000 + 1.2\,\mathrm{Re}^{0.66}}{1000 + 3.2\,\mathrm{Re}^{0.66}}\right)^{P}\left(\frac{Z}{D}\right)^{(0.35 + b/D)} \sin\theta^{1.2} \qquad \text{(Eq. 5.3)}$$

$$A = 14 + \frac{b}{D}\left(670\left(\frac{d}{D} - 0.6\right)^2 + 185\right)$$

$$\log B = 1.3 - 4\left(\frac{b}{D} - 0.15\right)^2 - 1.14\left(\frac{d}{D}\right)$$

$$P = 1.1 + 4\left(\frac{b}{D}\right) - 2.5\left(\frac{d}{D} - 0.5\right)^2 - 7\left(\frac{b}{D}\right)^4$$

$$Re = \frac{\rho n d^2}{\mu}$$

where Z [m], D [m], b [m], θ [-], and μ [Pa·s] show the reactor height, the reactor diameter, the paddle height , the paddle gradient, and the viscosity of the fluid, respectively. The required power consumption was estimated to be 0.151 kW/m^3-reactant from the above calculation.

5.2.2 $CaCO_3$ precipitation reactor

(Scale) The size of the precipitation reactor was estimated by the same methods used for the extraction reactor. A geometrically shaped reactor similar to the experimental apparatus was assumed. The reactor volume required was determined from the required $CaCO_3$ production rate, the retention time of the solution in the reactor, and the precipitation reaction rate. For this calculation, the empirical formula presented in chapter 4 was used.

(Capital cost) The capital cost for the precipitation reactor was estimated by the same methods used for the extraction process. Note that the thickness of the precipitation reactor is thinner that that of the extraction reactor because the CO_2 pressure in the precipitation reactor is lower.

(Power consumption) The power consumption from stirring in the precipitation reactor was estimated by the same methods used for the extraction process.

5.2.3 Silo for waste cement powder storage

Such silos are needed for storage and for feeding materials.

(Scale) The specifications of the required waste cement silo are determined from the annual throughput of waste cement powder. The required feed speed of the silo [t-waste cement/h] was calculated from the annual throughput, the number of operating days per year, and the operating hours per day.

(Capital cost) The capital cost of the silo was estimated by a power method based on the past records (3.0×10^8 JPY*, 10 t/h) of a Japanese electrical company (1 USD = 118 JPY at Feb. 21, 2006). The multiplier factor for the power method was assumed to be seven tenths. The capital cost for the silo is given by

$$\text{(The capital cost for the silo) [JPY]} \\ = 3.0 \times 10^8 \text{ [JPY]} \times (\text{feed rate [t-waste cement/h]} / 10 \text{ [t/h]})^{0.7} \qquad \text{(Eq. 5.4)}$$

(Power consumption) The power consumption of the silo was not considered.

5.2.4 Silo for storage of the $CaCO_3$ produced

(Scale) The specifications of the silo required for storage of the $CaCO_3$ produced is determined from the annual production of $CaCO_3$. The required feed speed of the silo [t-$CaCO_3$] was calculated from the annual production, the number of operating days per year, and the operating hours per day.

(Capital cost) The capital cost of the silo was estimated by the same method used for the waste cement silo. The capital cost for the silo is given by

$$\text{(The capital cost for the silo) [JPY]} \\ = 3.0 \times 10^8 \text{ [JPY]} \times (\text{feed rate [t-}CaCO_3\text{/h]} / 10 \text{ [t/h]})^{0.7} \qquad \text{(Eq. 5.5)}$$

(Power consumption) The power consumption of the silo was not considered.

5.2.5 CO_2 capturing facility

CO_2 will be captured from flue gas by an amine absorption / desorption process. In the process, the CO_2 in flue gas is chemically captured by alkanolamine as R. 5.1, and the captured CO_2 is recovered as R.5.2.

$$R-NH_2+H_2O+CO_2 \xrightarrow{311K} R-NH_3HCO_3 \qquad \text{(R. 5.1)}$$

$$R-NH_3CO_3 \xrightarrow{422K} R-NH_2+H_2O+CO_2 \qquad \text{(R. 5.2)}$$

(Scale) The CO_2 throughput is determined from the annual production of $CaCO_3$. The required recovery speed of CO_2 was calculated from the annual $CaCO_3$ production, the number of operating days per year, and the operating hours per day.

(Capital cost + Power consumption) For the capital cost and power consumption for CO_2 recovery using alkanolamine, cost estimations from the Chugoku Electric Power Corporation and Mitsubishi Heavy Industries were used. The value was calculated assuming CO_2 recovery by a real plant. Because detailed information of such estimations constitute industrial secrets for both corporations, only the recovery costs for several given recovery amounts were supplied. These values were summarized in table 5.1. Electrical power costs are included in these values.

Table 5.1. CO_2 recovery costs using the chemical absorption method

The CO_2 recovery costs are mostly in the range of 10,000 ~ 25,000 JPY/t-CO_2, and decrease with an increase of the amount of CO_2 recovered. Figure 5.2 shows the fitting for the formulation of the cost of capturing CO_2 as a function of the amount recovered

Figure 5.2. Fitting for the formulation of the cost of capturing CO_2 as a function of the amount recovered

From the fitting, the cost of capturing CO_2 is given by

$$(\mathrm{CO_2\ recovery\ cost}) = 10432 + 17127 \cdot \exp\left(-\frac{2470}{\mathrm{M_{CO2,\,year}}}\right) \quad [JPY/t-CO_2] \qquad \text{(Eq. 5.6)}$$

where $\mathrm{M_{CO2,\,year}}$ shows the annual amount of CO_2 recovered [t-CO_2/year]. From this relational equation, the lower limit of CO_2 recovery is about 10,000 JPY/t-CO_2, and contributes in a large part to the cost of concrete waste recycling.

5.2.6 CO_2 compressor

(Scale) The CO_2 that needs to be compressed is determined in the same way as determining the amount of CO_2 recovered. The specifications for the required CO_2 compressor were calculated from the annual production, the number of operating days per year, and the operating hours per day. The amount of CO_2 needing to be compressed is the same as the amount of recovered CO_2.

(Capital cost) The capital cost of the CO_2 compressor was estimated from the cost of an actual air compressor obtained from an interview with Ishikawajima-Harima Heavy Industries Co. (IHI). The capital cost of the air compressor is 15 million JPY (1,500 Nm^3-air/h), and a value of 50 million JPY (1,500 Nm^3-CO_2/h) was assumed as that the cost for the CO_2 compressor. Scaling-up was conducted by a power method, with the multiplier factor assumed to be seven tenths.

(Power consumption) The power consumption was assumed to be five times that of the air compressor; thus, 150×5 kW (IHI, 1,500 Nm^3-CO_2/h) was used. The power consumption was assumed to be proportional to the amount of CO_2 compressed.

Note: The ideally energy for gas compression

The ideal energy for the isothermal compression of an ideal gas is given by

$$E_{comp} = RT \ln \frac{p_1}{p_0} \qquad \text{(Eq. 5.7)}$$

where E_{comp} is the energy needed for ideal isothermal compression, R is a gas constant, T is temperature, and p_0 and p_1 are pre and post compression pressures, respectively.

5.2.7 Air compressor

In section 3.4, fine and pure $CaCO_3$ (8.4 μm by a volume based intermediate value, 99 wt%) could be obtained by bubbling N_2 in the precipitation reactor. Thus the air bubbling method (in a practical process, it is not necessary to use N_2) is considered to be an effective option for producing high-value added $CaCO_3$. Therefore, air compressor use was assumed.

(Scale) The throughput of air needed for bubbling was assumed to be one fifth of the required CO_2.

(Capital cost) For an estimation of the capital cost, the value of 15 million JPY (IHI, 1,500 Nm^3-air/h) was used as the base case value, and scaling-up was conducted by a power method, with the multiplier factor assumed to be seven tenths.

(Power consumption) The power consumption was estimated from the value of 150 kW (IHI, 1,500 Nm^3-air/h), and was assumed to be proportional to the amount of air compressed.

5.2.8 Pulverizer

(Scale) The specifications of the required pulverizer were calculated from the annual waste throughput, the pulverizing ratio of waste, the number of operating days per year, and the operating hours per day.

(Capital cost) For the estimation of the capital costs, a value of 70 million JPY (Kurimoto, 30 t-waste concrete/h) was used as the base case value, and scaling-up was conducted by a power method, with the multiplier factor assumed to be seven tenths.

(Power consumption) The power consumption was estimated from the value of 300 kW (Kurimoto, 30 t-waste concrete/h), and was assumed to be proportional to the amount of air compressed.

Note: Energy for pulverization

The energy for pulverization is empirically given by Bond's law;

$$E_{pul} = k_B \left(\frac{1}{\sqrt{Dp_2}} - \frac{1}{\sqrt{Dp_1}} \right) \qquad \text{(Eq. 5.8)}$$

where E_{pul} shows the energy for pulverization, k_{B} is a constant inherent in each material, and D_{p1} and D_{p2} are the pre and post, respectively, particle diameters.

5.2.9 Waste water treatment facility

The water necessary for the extraction reaction can be recycled after the precipitation operation. Treating the water would be required because some unnecessary components that are soluble in water would accumulate after a number of reuse cycles. The cost for wastewater treatment was estimated from the amount of wastewater and the unit cost for wastewater treatment with 100 cycles of water reuse before treatment.

(Scale) The treatment amount was assumed to be 0.01 (100 cycles) times the amount of water required for the extraction process.

(Capital cost) The capital cost was assumed to be 0, because the use of an existing facility was assumed.

(Power consumption) The electrical power cost was included in the net cost for wastewater treatment: 205 JPY/m^3 (actual data from the Chugoku Electric Power Corporation).

5.3 Estimation of the cost of the proposed recycling plant

For the revenue and cost of the proposed recycling plant, grant money, the interest on borrowings and a variety of taxes such as fixed property taxes, were not considered.

Revenue:

(I) Revenue from the sale of $CaCO_3$
(II) Revenue from the sale of extracted residues

Costs:

(III) Employment, (IV) Materials, (V) Depreciation
(VI) Maintenance,
(VII) Utilities (electricity and water),
(VIII) Wastewater treatment, (IX) Waste disposal,
(X) Testing, (XI) capturing CO_2

Detailed methods for the estimations of each item are summarized below.

5.3.1 Revenue from the sale of $CaCO_3$

The revenue from selling $CaCO_3$ was calculated from the unit price of $CaCO_3$ on the Japanese market and amount of $CaCO_3$ produced in the recycling plant. Table 5.2 summarizes the results of market research in respect to $CaCO_3$.

Table 5.2. Market research in respect to calcium carbonate

Light calcium carbonate is chemically precipitated $CaCO_3$ by recrystallization, while heavy calcium carbonate is finely pulverized limestone. The purity of high-quality heavy calcium carbonate is 98 ~ 99 wt%.

In this study, based on the results from section 3.4, the unit cost of $CaCO_3$ produced was assumed to be 15 JPY/kg for $CaCO_3$ without recrystallization, and 27 JPY/kg for the $CaCO_3$ with recrystallization.

5.3.2 Revenue from the sale of extracted residues

After carbonic acid treatment of the concrete waste, residue remains. The amount of residue (mainly silica dioxide) extracted is very large, and its treatment strongly affects the feasibility of the recycling process. In this study, the sale price per unit of the extracted residue was assumed to be 100 JPY/t (obtained from an interview with Kajima Construction Company). In the worst case scenario for extracted residue it is treated as industrial waste, with a final disposal of 4,500 JPY/t (obtained from an interview with the Kajima Construction Company).

5.3.3 Employment costs

The total employment cost for the recycling plant was assumed to be 56 million JPY/year. The unit cost for employment was assumed to be 8 million JPY/year/person. A detailed breakdown of this cost is summarized in table 5.3.

Table 5.3. Employment costs for the proposed recycling plant

5.3.4 Material costs

The cost of accepting waste cement was allocated to the material costs. In Japan, crushed waste concrete is sold as products such as recycled stone and sand. Thus, to obtain waste concrete, the company running the recycling plant must usually pay an acceptance cost for waste concrete. The acceptance cost per unit was assumed to be 2,000 JPY/t. If the company running the proposed recycling plant can be certified as an intermediate waste processor, it then becomes possible to “onerously” accept the waste cement, and the acceptanse cost then comes from the demolition company and is allocated as revenue; however, this is thought difficult in the Japanese situation.

5.3.5 Depreciation cost

The operational span of the proposed recycling plant was assumed to be 15 years, and depreciation cost were calculated as 90 % of the total capital cost divided by 15. The total capital cost is the sum of the plant cost, the cost of construction of the facilities, and the costs of heavy machinery. The plant cost was estimated by the method mentioned in section 5.2.10, and the cost for construction of the facilities was assumed to be 25 % of the plant cost. The cost of heavy machinery was set as 30 million JPY/year.

5.3.6 Maintenance costs

The maintenance factors for the recycling plant were assumed as those set out in table 5.4. Maintenance costs were calculated from the various capital costs times each of the maintenance factors.

Table 5.4. Maintenance factors assumed for the proposed recycling plant

5.3.7 Utility costs (electricity and water)

The unit electricity cost was assumed to be 10 JPY/kWh (the basic electricity rate was included in this value). Power consumption of the plant was estimated as in section 5.2.11, and 10 % of that was added to the total power consumption for lighting and other power consumptions. The unit cost for water was assumed to be 60 JPY/m^3.

5.3.8 Wastewater treatment costs

The unit cost for wastewater treatment was assumed to be 205 JPY/m^3 (refer to section 5.2.7), and was calculated from the unit cost times the amount treated.

5.3.9 Waste disposal costs

No waste is generated from the proposed recycling plant, so waste disposal costs are disregarded. However, if the extracted residue is treated as industrial waste, then the waste disposal cost is considered to be 4,500 JPY/t.

5.3.10 Testing costs

Testing costs were disregarded in this study.

5.3.11 CO_2 capturing costs

CO_2 capturing costs were estimated using the relational equation;

$$(\mathrm{CO_2\ recovery\ cost}) = 10432 + 17127 \cdot \exp\left(-\frac{2470}{\mathrm{M}_{\mathrm{CO2,\,year}}}\right) \quad [JPY/t-CO_2] \qquad \text{(Eq. 5.6)}$$

where $\mathrm{M}_{\mathrm{CO2,\,year}}$ shows the annual amount of CO_2 recovered [t-CO_2/year]. The chemical absorption / desorption process was assumed as the capturing method.

The process design of the proposed waste concrete recycling plant was conducted, and based on the assumptions noted above an economical and environmental impact assessment is carried out in the next chapter.

References

Fuji Chimera Research Institute, 2004, "2004 nen bihunntai sijou no genjou to syouraitennbou" (in Japanese), Japan.

Society of Chemical Engineers, 1999, ed. Kagaku Kogaku Binran (in Japanese), 6th ed., Maruzen, Tokyo, Japan.

Appendix III

III. 1 Calcium carbonate

World market trends for calcium carbonate are summarized. The market for calcium carbonate is a worldwide one. Especially, nanosized calcium carbonate, due to its positive effects on strength or transparency, is a necessary material in the plastic and rubber industries (Global Industry Analysis, 2004).

Figure III.1. Size of the market for calcium carbonate

Figure III.1 demonstrates variations in the size of the market for $CaCO_3$. The report of the Global Industry Analysis predicts that the market for $CaCO_3$ will expand greatly in the near future, and that the present worldwide market size is about 20 Mt, with 2 Mt for Japan. Table III.1 shows the results of $CaCO_3$ market trends research in Japan, and table III.2 summarizes the application and selling volumes from the Fuji Chimera Research Institute (2004).

Table III.1. Calcium carbonate market trends

Table III.2. Calcium carbonate applications and selling volumes

Contrarily, in this research the demand for both light and heavy calcium carbonate is predicted to decrease. However, a contributing factor for the decrease in demand for light calcium carbonate is considered to be self-production by industrial consumers. Thus, a decrease in the demand is apparent. Furthermore, the demand for high-value added products is predicted to increase (Fuji Chimera Research Institute, 2004).

The prices for calcium compounds and the amounts produced in Japan are summarized in table III.3.

Table III.3. Prices of calcium compounds and amounts producted in Japan (The Chemical Daily, 2000)

III. 2 Other sources of calcium in Japan

Table III.4 demonstrates the amount of calcium containing waste generated in Japan. The amount of iron slug generated is the largest portion, and it has a high calcium-containing rate. However, a large portion of the iron slug produced is currently used as a raw material in the cement industry. The amount of waste shell generated annually is small (1.0 Mt annually); however, its calcium-containing rate is high and so it is considered a useful calcium source.

Table III.4. Amount of calcium containing waste generated annually in Japan

III. 3 Sources of intensive CO_2 emissions

Table III.5 contains data of the sources of intensive CO_2 emissions in Japan. Thermal power plants have the largest amounts of emissions, followed by the iron, petrochemical and cement industries also with large CO_2 emissions. The CO_2 concentration in flue gas is about 10 ~ 30 %. Table III.6 shows the basic units of each gas emitted at each type of power plant, and table III.7 shows the various compositions of gases emitted with power generation at coal-fired thermal power plants.

Table III.5. Data of sources of intensive CO_2 emissions in Japan

Table III.6. Basic units of gases emitted at each type of power plant

Table III.7. Compositions of gasses emitted during power generation at coal-fired thermal power plants

References

The Chemical Daily, 2000, "13700 no kagaku shouhin" (in Japanese), Tokyo, Japan.

Fuji Chimera Research Institute, 2004, "2004 nen bihunntai sijou no genjou to syouraitennbou" (in Japanese), Japan.

Global Industry Analysis, 2004, "Calcium Carbonate", USA.

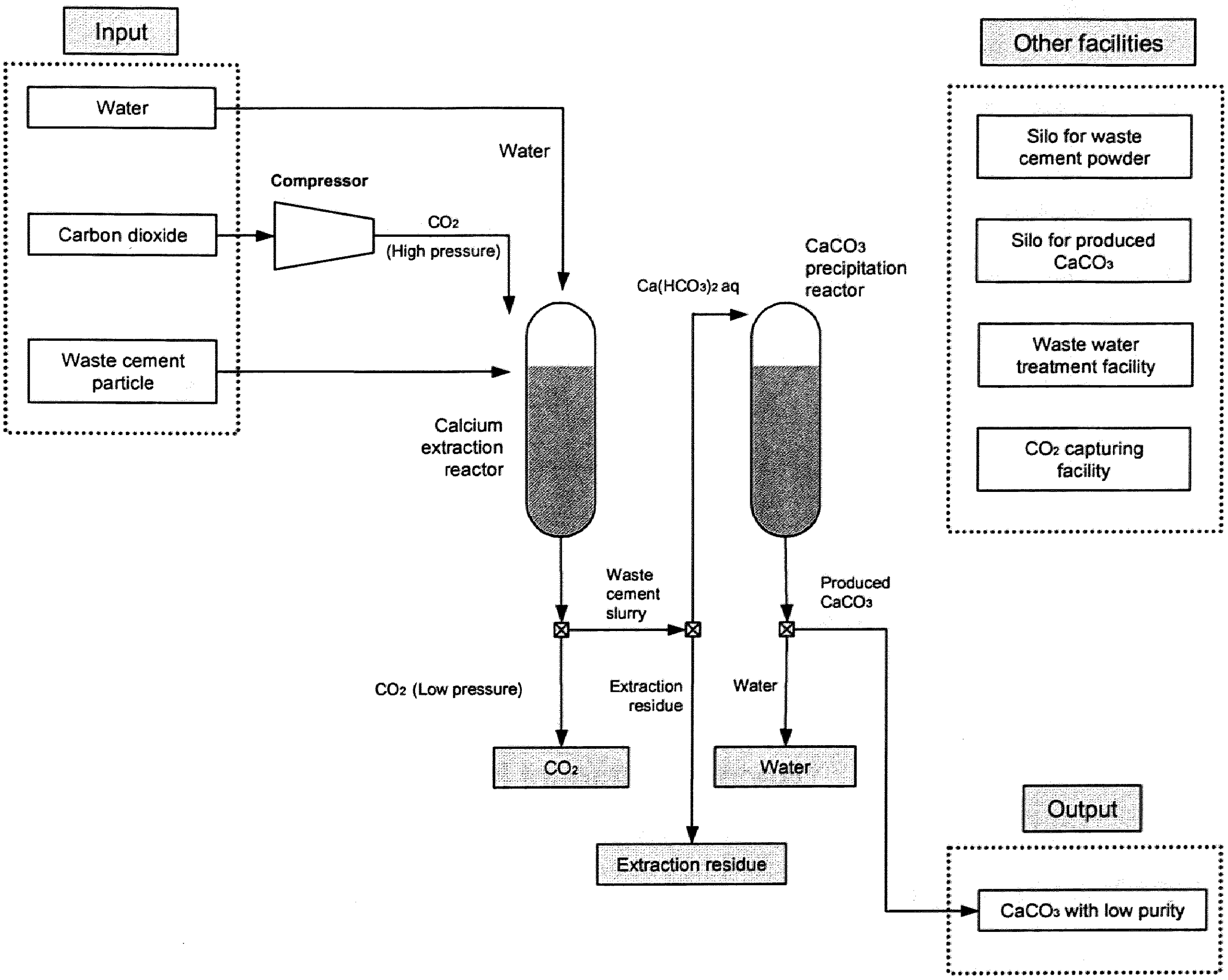

Figure 5.1. An example of the composition of the proposed concrete waste recycling plant

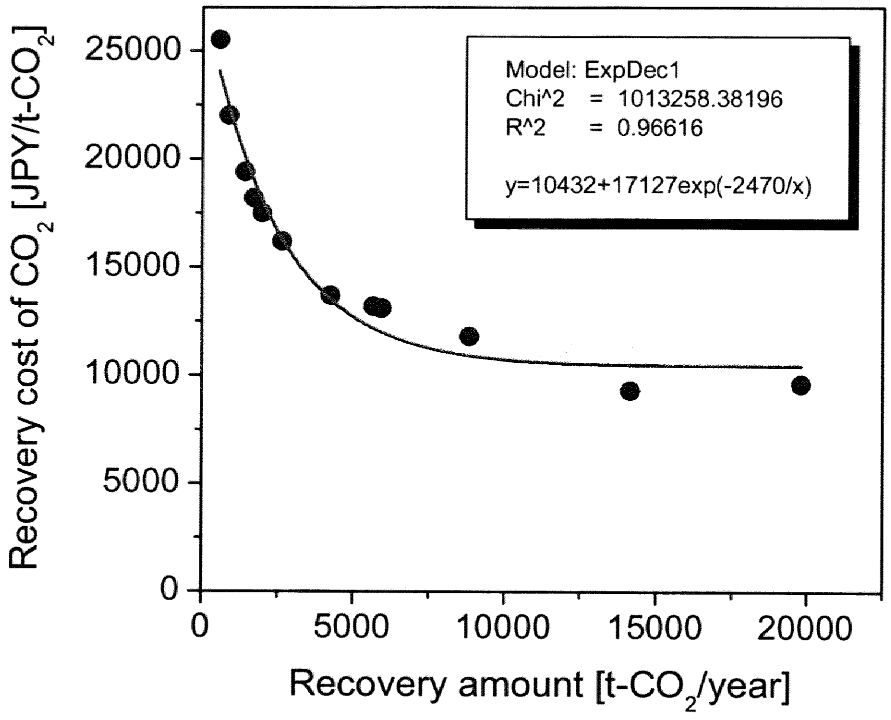

Figure 5.2. Fitting for the formulation of the cost of capturing CO_2 as a function of the amount recovered

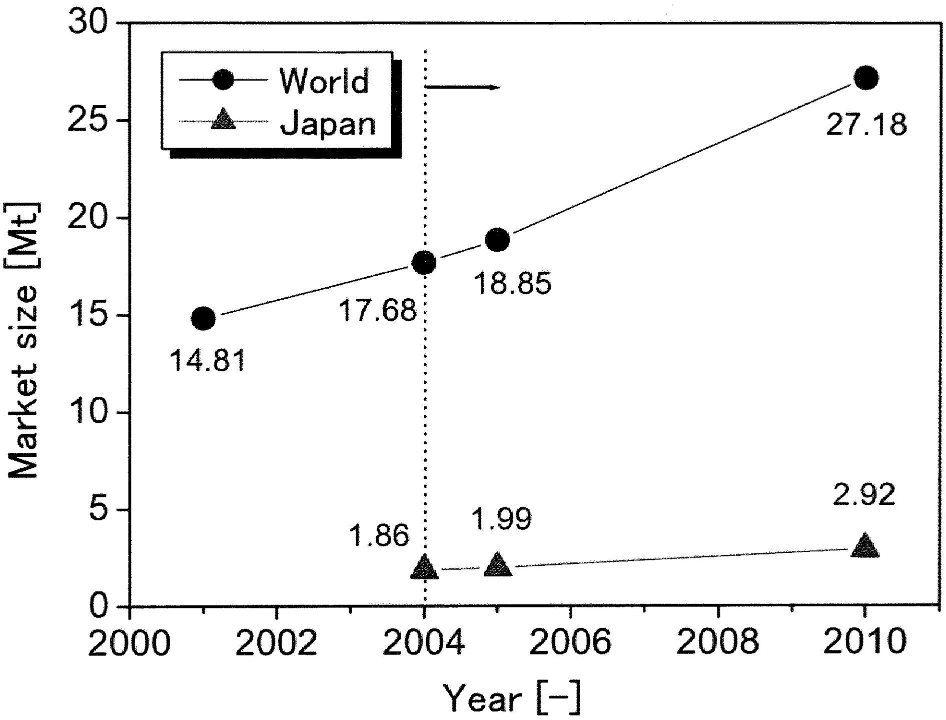

Figure III.1. Size of the market for calcium carbonate (ref. Global Industry Analysis, 2004)

Table 5.1. CO_2 recovery costs using the chemical absorption method (from an interview with the Chugoku Electric Power Corporation)

CO_2 recovery amount [t-CO_2/year]	Recovery cost [JPY/t-CO_2]	Contribution of CO_2 recovery cost per ton of $CaCO_3$ [JPY/t-$CaCO_3$]
566	25,500	11,000
884	22,000	9,400
1,414	19,400	8,500
1,697	18,200	8,100
1,980	17,500	7,600
2,652	16,200	7,100
4,243	13,700	6,000
5,657	13,200	5,800
5,940	13,100	5,800
8,839	11,800	5,200
19,800	9,600	4,200
14,143	9,300	4,100

*1 USD = 118 JPY at Feb. 21, 2006

Table 5.2. Market research in respect to calcium carbonate (ref. Fuji Chimera Research Institute, 2004)

	Product	Particle size [μm]	Price [JPY/kg]	Sales volume (2004) [Mt]	Japanese maker
Light $CaCO_3$	Staple product	1.0 ~	27 (for paper: 2 ~ 5 μm)	198	6
	Semi colloid product	0.1 ~ 1.0	37 (for paper: 0.1 ~ 0.9 μm)	209	5
	Colloid product	~ 0.1			
Heavy $CaCO_3$	Dry	1 ~ 15	3 μm 15 ~ 20 4 μm 13 ~ 18 5 μm 11 ~ 16	1,001	9

Table 5.3. Employment costs for the proposed recycling plant

	Workforce number	Total workforce number	Unit cost [10^6 JPY/year]	Employment cost [10^6 JPY/year]	Remarks
Operator, Monitor	1	4	8.0	32.0	Three shift
Heavy machine worker	2	2	8.0	16.0	Day shift
Indirect worker	1	1	8.0	8.0	Day shift
Total	-	7	-	56	-

Table 5.4. Maintenance factors assumed for the proposed recycling plant

Facilities	Maintenance factor [%]
Plant	10
Construction facilities	1.5
Heavy machine	3

Table. III.1. Calcium carbonate market trends

Product		Growth factor	Growth constraint	Remarks
Light $CaCO_3$	Staple product	◆Necessary for paper production ◆Low cost ◆Demand in Asia is increasing	◆Self producing by paper maker ◆New market cannot be found ◆Relocation of consumer factory to abroad	◆Market size is decreasing by self producing ◆Transition to staple product ◆High value added product investigation is needed
	Semi colloid product, Colloid product	◆Necessary for resign and paint ◆Demand generation by microparticulation ◆Demand in Asia is increasing	◆Transition to staple product ◆Relocation of consumer factory to abroad	
Heavy $CaCO_3$	Dry	◆Necessary for resign and paint ◆Constant demand ◆Import amount is small due to its low cost	◆ New market cannot be found ◆ Relocation of consumer factory to abroad	◆Demand is decreasing

Table. III.2. Calcium carbonate applications and selling volumes

(a) Applications and its functions

Application	Function	Remark
Plastic	Improvement in strength, stability, mobility, dispersibility Addition of functionality Low cost	Colloid product is often used in underlined applications
Rubber	Improvement in workability Addition of functionality. Low cost	
Paint	Adjustment of viscosity, paint workability Joint searing Addition of functionality	
Paper (filler)	Whitening Improvement in storage stability (alkalinize) Low density	
Paper (coating)	Addition of optical function Printability	
Agriculture	Water-dispersible function for pesticide Soil conditioner	

(b) Application and selling volume (2003)

Product			Selling volume (2003) [Mt]	Fraction [wt%]
Light $CaCO_3$	Staple product	Paper	115	58.7
		Rubber	23	11.7
		Resin	18	9.2
		Paint	8	4.1
		Others	14,000	7.1
		Export	18,000	9.2
	Colloid product	Paper	73,000	34.8
		Rubber	55,000	26.2
		Resin	44,000	21
		Paint	10,000	4.8
		Others	9,000	4.2
		Export	19,000	9

Table III.3. Prices of calcium compounds and amounts producted in Japan (The Chemical Daily, 2000)

Compounds	Price
Calcium silicate ($CaSiO_3$)	1.5 JPY/kg (20 kg)
Calcium carbide (CaC_2)	105 ~ 120 JPY/kg (10t)
Calcium chloride ($CaCl_2$)	50 ~ 56 JPY/kg (purity: 72% ~ , due to dihydrate interfusion)
Calcium (Ca)	1,000 ~ 1,300 JPY/kg (500 kg); Production 300 t (1998)
Calcium sulfite ($CaSO_3 \cdot 1/2H_2O$)	1,500 JPY/kg; Production 200 t (1998)
Calcium peroxide (CaO_2)	800 JPY/kg
Calcium hypophosphate ($Ca(H_2PO_2)_2$)	3,000 JPY/kg
Calcium oxide (CaO)	18 ~ 22 JPY/kg (truck road); Production 7.65 Mt (1998)
Calcium hydroxide ($Ca(OH)_2$)	23 ~ 28 JPY/kg (truck road); Production 1.81 Mt (1998)
Calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$)	260 ~ 280 JPY/kg
Calcium carbonate ($CaCO_3$)	Light: 42 ~ 47 JPY/kg (10 t); Production 0.42 Mt (1998) Heavy: 20 ~ 35 JPY/kg (10 t); Production unkown
Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$)	5 ~ 6 JPY/kg (10 t); Production 5.30 Mt, Import 2.93 Mt (1998)
Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)	10,000 JPY/kg; Production 30 t (1998)
Calcium acetate ($Ca(CH_3COO)_2 \cdot H_2O$)	550 JPY/kg (for industrial use), 830 JPY/kg (first); Production 500 t (1998)

Table III.4. Amount of calcium containing waste generated annually in Japan

	Main component	Amount [Mt/year]	Ca fraction [wt%]	Ca available amount [Mt/year]
Iron slug	$3CaO \cdot 2SiO_2$ $CaO \cdot SiO_2$ $3CaO \cdot Fe_2O_3$	36.4	18 ~ 39	7.0 ~ 14.0
Waste concrete	$Ca(OH)_2$ $3CaO \cdot 2SiO_2 \cdot 3H_2O$	35.0	10	3.5
Waste shell	$CaCO_3$	About 1.0	38 ~	0.38 ~

Table. III.5. Data of sources of intensive CO_2 emissions in Japan

Intensive emission source	CO_2 emission amount [Mt/year]	CO_2 concentration in flue gas [%]	Basic unit of CO_2 emission
Thermal power plant	376.6	10 ~ 13	0.4~0.5 [kg-CO_2/kWh]
Cement plant	58.6	About 20	0.770 [t-CO_2/t-cement]
Steel plant	178.0	About 25	1.7 [t-CO_2/t-basic steel]
Petrochemical plant	69.0	About 30 ~ 50	1.17 [t-CO_2/t-petrochemicals]

Table III.6. Basic units of gases emitted at each type of power plant

Fuel type		Basic unit of CO_2 emission [kg-CO_2/kWh] (fuel origin)	Basic unit of flue gas [Nm^3/h/kWh] (wet)	CO_2 concentration in flue gas [vol%] (wet)
Coal		0.887	3 ~ 4	12 ~ 14
Oil		0.704	2 ~ 3	11 ~ 12
LNG	Conventional	0.478	2 ~ 3	8 ~ 9
	Combined	0.408	5 ~ 8	3 ~ 5

Table III.7. Compositions of gasses emitted during power generation at coal-fired thermal power plants

	unit	Power generation loading [%]			
		100	75	50	30
CO_2		13	12	11	10
O_2		4	5	6	8
N_2	Vol.%	About 73	←	←	←
CO		—	—	—	—
H_2O		About 10	←	←	←

6. Evaluation of the proposed concrete waste recycling process

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6. Evaluation of the proposed concrete waste recycling process

In the previous chapters, the process design for the proposed concrete waste recycling process was presented, and methods of estimation concerning revenues and costs were summarized. In this chapter, some example cases are presented based on current Japanese social and economic circumstances, and process evaluation for each case is conducted.

6.1 Case establishment

6.1.1 Assumptions

In this study, it was assumed that recycling plants as proposed are set throughout the nation and recycle the all the waste concrete generated in Japan. The number of plants introduced is discussed in section 6.1.3. The annual amount of waste concrete recycled per unit recycling plant was calculated from the total amount of waste concrete generated in Japan and the number of the plants introduced, while the economic feasibility and environmental impact of one recycling plant was investigated. Further, the total impact of introducing a recycling plant was assessed.

6.1.2 Location of recycling plants

The best location for one of the proposed recycling plants is considered to be near a thermal power plant. This is because there will be enough space to introduce the plant and the wastewater treatment facility (for flue gas desulfurization process). Furthermore, it is advantageous that waste heat is available to heat the reactant.

6.1.3 Establishing the annual amount of waste concrete recycled per unit plant

There are about 100 thermal power plants in Japan, with locations somewhat unevenly distributed near seaside areas. Table 6.1 and 6.2 show the numbers of steel and cement plants and amounts of their CO_2 emissions: the main intensive CO_2emission sources in Japan. Steel plants locate at about 100 sites, and about 40 for cement plant in Japan. Both types of plants are evenly distributed throughout Japan.

Table 6.1. Regional data of numbers and CO_2 emissions of steel plants

Table 6.2. Regional data of numbers and CO_2 emissions of cement plants

On the other hand, the amount of waste concrete generated annually in Japan is 35 Mt (actual data for 2002, Ministry of Land, Infrastructure and Transport, 2004). The amount generated varies seasonally, and has a peak at the end of each business year. To stabilize the rate of recycling waste concrete, a storage silo was assumed as part of a recycling plant. Figure 6.1 shows waste concrete generation distribution by location, and table 6.3 shows waste concrete generation, reuse, and the amount for final disposal for each prefecture in Japan.

Figure 6.1. Waste concrete generation distribution in Japan by location

Table 6.3.a Waste concrete generation, reuse, amount for final disposal in each prefecture in Japan (Hokkaido ~ Mie)

Table 6.3.b Waste concrete generation, reuse, amount for final disposal in each prefecture in Japan (Fukui ~ Okinawa)

The amount of waste concrete generated is especially large; however, in principle it is proportional to the various area populations. Waste concrete now generated is crushed and classified, and then sold as roadbed material at about 2,400 intermediate treatment sites (ref. figure 1.3). The average amount of concrete waste treated at one intermediate treatment site is a bout 15,000 t/year (= 35 Mt/2400 sites).

Based on th current Japanese situation, it is considered that a figure of 100 ~ 1000 of the proposed waste concrete recycling plant installations would be realistically needed.

For this number, the amount of waste concrete for treatment at each recycling plant is calculated to be 30,000 (= 30 Mt/1000 sites) ~ 300,000 (= 30 Mt/100 sites) t/year.

6.1.4 The calcium conversion rate in waste cement

It is preferable that wherever possible the rate of conversion to $CaCO_3$ of the calcium contained within waste cement behigh, because the proposed process involves one of recycling waste cement. However, a higher conversion rate of calcium may lead to high operational costs and difficult operational conditions. From the results in section 3.2.3, the maximum conversion rate of calcium was estimated to be about 80%. In this chapter, the calcium conversion rate was set at 80%, and for comparison, cases of a conversion rate of 50% were also examined.

6.1.5 Example cases

Based on section 6.1.3 and 6.1.4, a total of 6 example cases are summarized in table 6.4, and the schematic drawing of a proposed recycling plant for the base cases is shown in figure 6.2. For each case, the introduction of a recrystallization process was assumed to produce high-purity $CaCO_3$. Cases without the recrystallization process were also investigated in section 6.1.6.1.

Table 6.4. Example cases

Figure 6.2. The schematic drawing of a proposed recycling plant for the example cases

6.1.6 Other cases investigated

The following three situations were also investigated in addition to the example cases; (I) cases without the recrystallization process of $CaCO_3$ (reactor sort: 4 to 2), (II) cases using pure water instead of tap water (unit cost of water: 60 to 200 JPY/m^3), and

(III) cases assuming revenue from the effects of CO_2 emission reduction by the recycling plant (100 USD/t-CO_2 = 10,500 JPY/t-CO_2*).

* 1 USD = 105 JPY was assumed for just this transaction

6.1.6.1 Cases without the recrystallization process for recrystallization of $CaCO_3$

Based on the results of section 5.3.1, the unit cost of the $CaCO_3$ produced was assumed to be 15 JPY/kg for $CaCO_3$ without recrystallization, and 27 JPY/kg for $CaCO_3$ with recrystallization. High-purity $CaCO_3$ can be obtained through the recrystallization process; however, re-solution and recrystallization reactors are needed for this process; thus, while the revenue from the sale of $CaCO_3$ increases, the capital cost of achieving the high-purity also increases.

6.1.6.2 Cases using pure instead of tap water

The feasibility for cases using pure instead of tap water was investigated; the unit cost for water changed from 60 JPY/m^3 to 200 JPY/m^3.

6.1.6.3 Cases assuming revenue from the effects of CO_2 emission reductions

The proposed waste concrete recycling process has the effect of reducing CO_2 emissions because CO_2 is consumed in the production of $CaCO_3$. For these cases, the revenue achieved from this effect was considered to be 100 USD/t-CO_2 (= 10,500 JPY/t-CO_2), and the economic feasibility was investigated.

6.2 Evaluation of the proposed recycling process

6.2.1 Material flows and operational conditions

The material flow for the base cases (1-a ~ 2-c) are summarized in table 6.5. Total material flow in Japan for cases 1 and 2 is also shown in the table. The operational conditions, such as reaction time, reactant volume and operation pressure are shown in table 6.6. The operational hours and days were assumed to be 24 hours per day 300 days per year.

Table 6.5. Lists of material flows and operational conditions for the example cases

Table 6.6. Operational conditions for the example cases

6.2.2 Economic evaluation

6.2.2.1 Economic evaluation for example cases

The capital costs and electricity consumption, basic data for the economical feasibility study, are shown in table 6.7 and 6.8. Data demonstrate the value for each recycling plant unit.

Table 6.7. Capital costs of the recycling plant for the base cases

Table 6.8. Electricity consumption of the recycling plant for the example cases

From these basic data, a breakdown of revenue and costs for the proposed waste concrete recycling plant is summarized in table 6.9.

Table 6.9. Breakdown of revenue and costs of the proposed waste concrete recycling plant

The economical feasibility of the recycling plant improves with an increase ijn the annual amount of waste concrete treated; this is due to the advantages of scale, especially in respect to capital and CO_2 recovery costs. For case 1 (conversion rate of calcium set at 50 %), the recycling plant is not economically feasible; but for case 2 (80%), only case 2-b (treatment amount set at 90,000 t/year) and 2-c (300,000 t/year) are feasible.

Table 6.10 shows the total waste concrete recycling cost in Japan (for recycling 35 Mt of waste concrete), treatment cost per unit waste cement, and the CO_2 sequestration cost.

Table 6.10. Total cost of recycling waste concrete, treatment cost per unit waste cement, and the CO_2 sequestration cost

The total waste concrete recycling cost relies on that the same amount of grant money is supplied to waste concrete treatment, and so concrete recycling can be carried out by the proposed recycling process. CO_2 sequestration costs show the cost needed for CO_2 consumption in the process. As noted above, the proposed process has a CO_2 emission reduction effect; the potential of the process is now 1.65 Mt/year in Japan, and the sequestration cost is highly competitive against other sequestration options.

6.2.2.2 Economic evaluation of the other cases

6.2.2.2.1 Cases without the process for recrystallization of $CaCO_3$

Table 6.11 shows a breakdown of revenue and costs for the proposed waste concrete recycling plant without the process for recrystallization of $CaCO_3$, and figure 6.3 shows the plant composition in this case. In these cases, the re-solution and the recrystallization reactors were removed from the plant costs.

Table 6.11. Breakdown of revenue and costs for the proposed waste concrete recycling plant without the process for recrystallization of $CaCO_3$

Figure 6.3. Schematic drawing of the recycling plant without the process for recrystallization of $CaCO_3$

In the case without the process for recrystallization of $CaCO_3$, the capital cost of the plant and the revenue from the sale of the $CaCO_3$ produced decreases. In these cases, the decrease in the revenue is very large, and for all 6 cases the recycling process was found not economically feasible.

6.2.2.2.2 Cases using pure instead of tap water

In this section, cases using pure water (200 JPY/m^3) for the reaction instead of tap water (60 JPY/m^3) were investigated. The results of the estimation are summarized in table 6.12. The plant compositions for these cases were the same as in figure 6.2.

Table 6.12. Breakdown of revenue and costs for the proposed waste concrete recycling plant using pure water

The influence of pure water use on plant feasibility was small, with the cost increase for the plant amounting to only about 1.0 million JPY per year.

6.2.2.2.3 Cases assuming revenue from the effect of CO_2 emission reduction

The proposed waste concrete recycling process has the effect of reducing CO_2 emissions, because CO_2 is consumed in the $CaCO_3$ precipitation reaction. In these cases, the revenue produced by this effect was considered to be 100 USD/t-CO_2 (= 10,500 JPY/t-CO_2), and the economic feasibility was investigated. The results of this estimation are summarized in table 6.12. The plant composition is the same as in figure 6.12 for these cases.

Table 6.13. Breakdown of revenue and costs for the recycling plant for cases considering the revenue from CO_2 emission reduction

In cases where revenue is obtained from the effect of CO_2 emission reduction, the income of a recycling plant unit increases by 10 ~ 100 million JPY/year, and the feasibility of the process is improved. Thus, the proposed recycling process is considered to be a competitive CO_2 sequestration process.

6.2.3 Environmental impact assessment

In this section, the environmental impacts caused by introducing the recycling plants were considered. Table 6.14 demonstrates the amount of waste reduced, power consumption, and the amount of the CO_2 emission reduction from introducing the process. Note that these results represent the total influence in Japan for case 2.

Table 6.14. Environmental impact of the proposed recycling process

The amount of the waste reduction is equivalent to the amount of waste concrete treated. The proposed process can recycle all the waste concrete generated in Japan. Furthermore, 1.65 Mt of CO_2 can be sequestrated in the form of stable carbonate. The amount of water consumed is not so large compared to that in the wet flue gas desulfurization process.

From the viewpoint of material circulation, the significance of the proposed process is that it makes it possible to economically recycle concrete waste. Figure 6.4 and 6.5 illustrate the annual material flows of concrete related materials, and of the calcium in wastes in Japan, respectively.

Figure 6.4. Annual material flow of concrete related materials in Japan

Figure 6.5. Annual material flow of calcium in wastes in Japan

Large amounts of materials are used in the production of concrete, and huge amounts of concrete have been accumulated in Japanese cities (figure 6.4). However, waste concrete and other calcium containing waste is now difficult to be effectively reused, despite its high chemical potential. These wastes have only been reused as roadbed materials or for civil engineering uses. These treatments are effectively the same as landfills from the viewpoint of resource circulation. Furthermore, the amount of waste concrete generated in Japan is predicted to increase; thus, the proposed recycling process will be of great importance in respect to this problem.

Reference

Ministry of Land, Infrastructure and Transport, 2004, “Heisei 14 nendo kensetsu hukusanbutsu jittai tyousa kekka” (in Japanese).

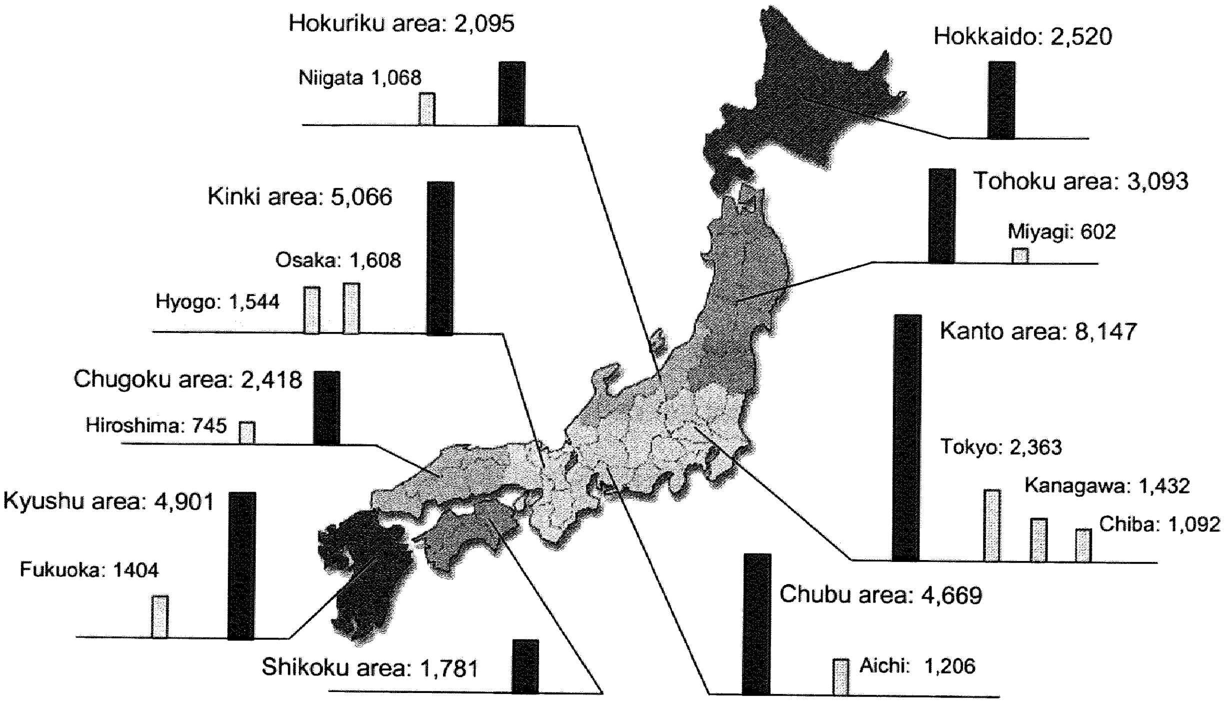

Figure 6.1. Waste concrete generation distribution in Japan by location (ref. Ministry of Land, Infrastructure and Transport, 2004)

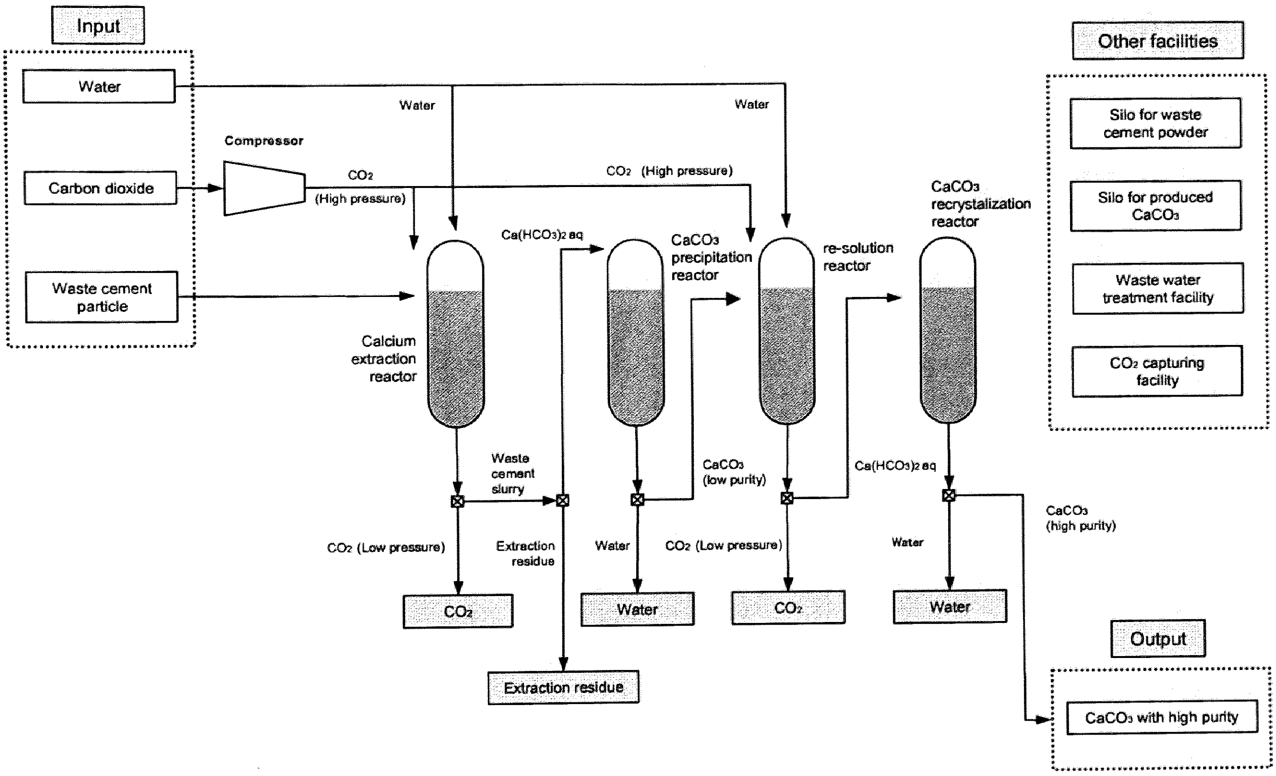

Figure 6.2. The schematic drawing of a proposed recycling plant for the example cases

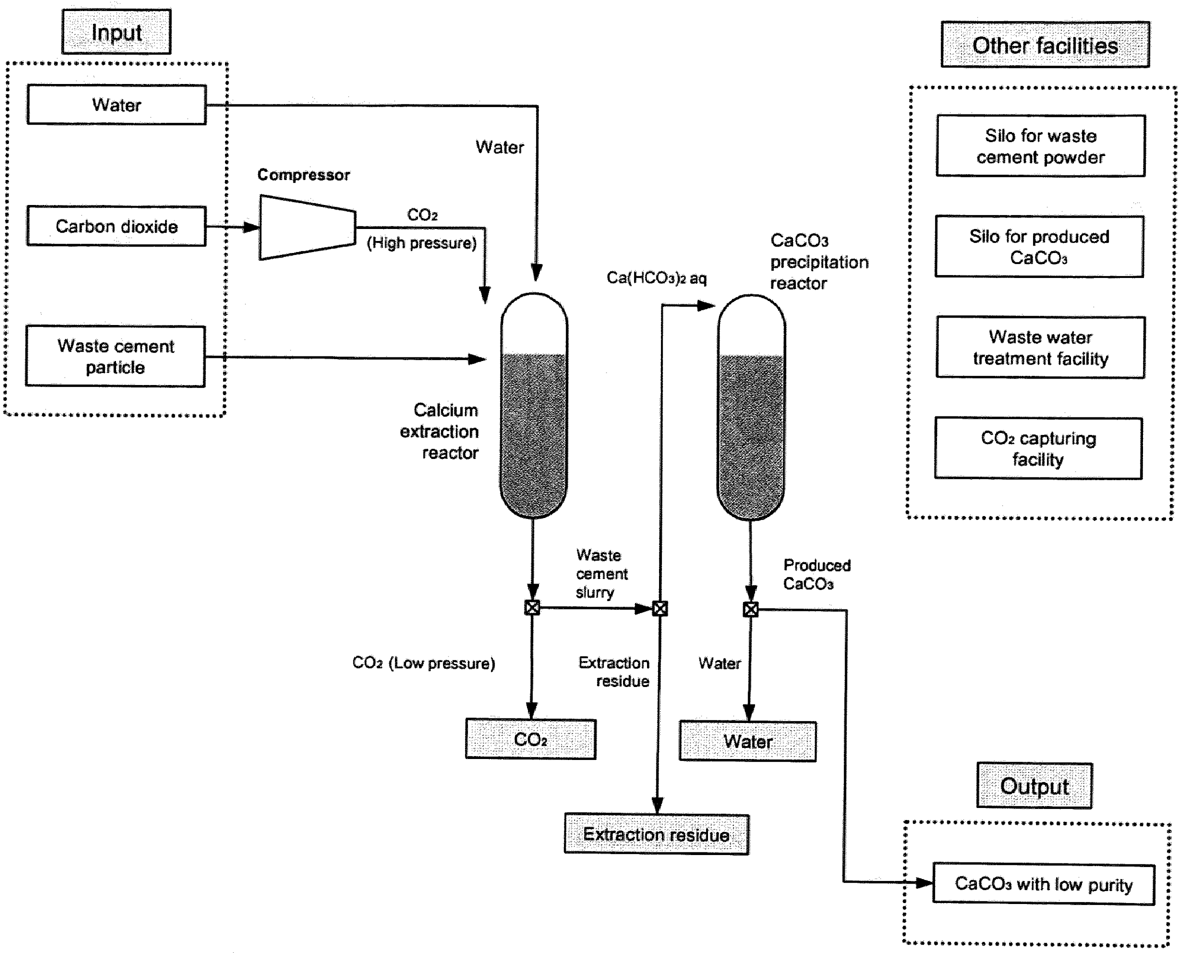

Figure 6.3. Schematic drawing of the recycling plant without the process for recrystallization of $CaCO_3$

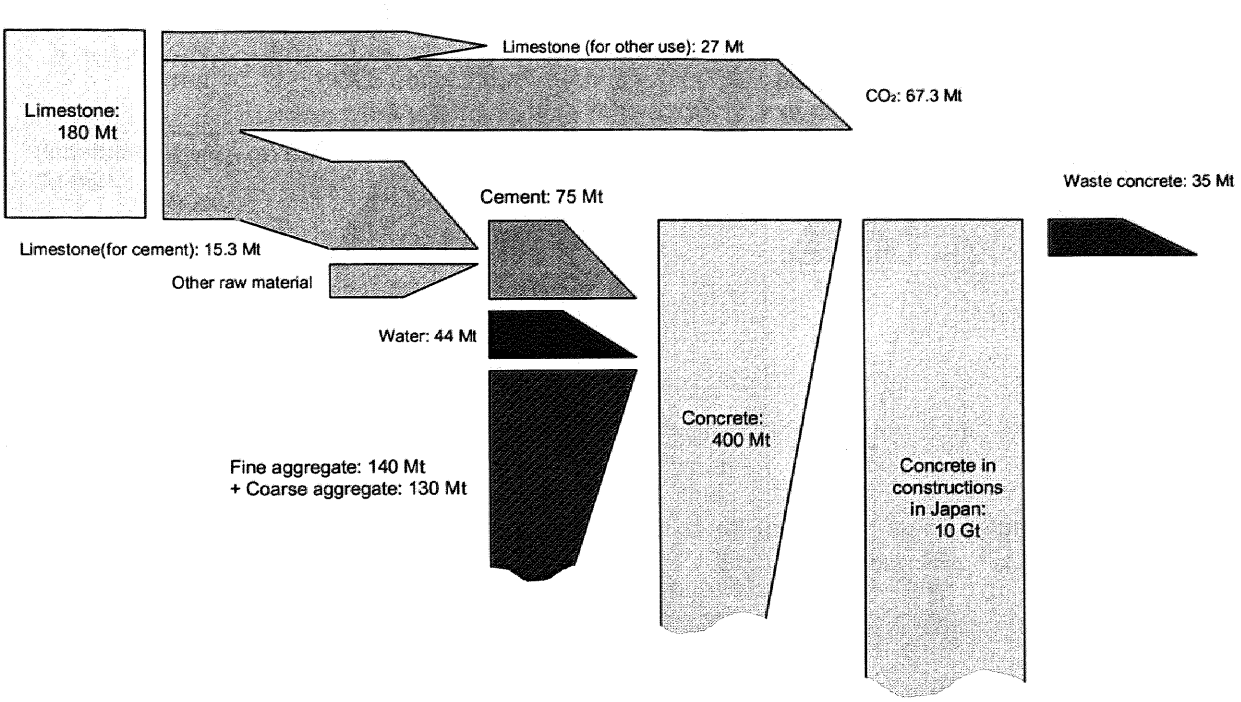

Figure 6.4. Annual material flow of concrete related materials in Japan. The width of each arrowed line is proportional to its amount.

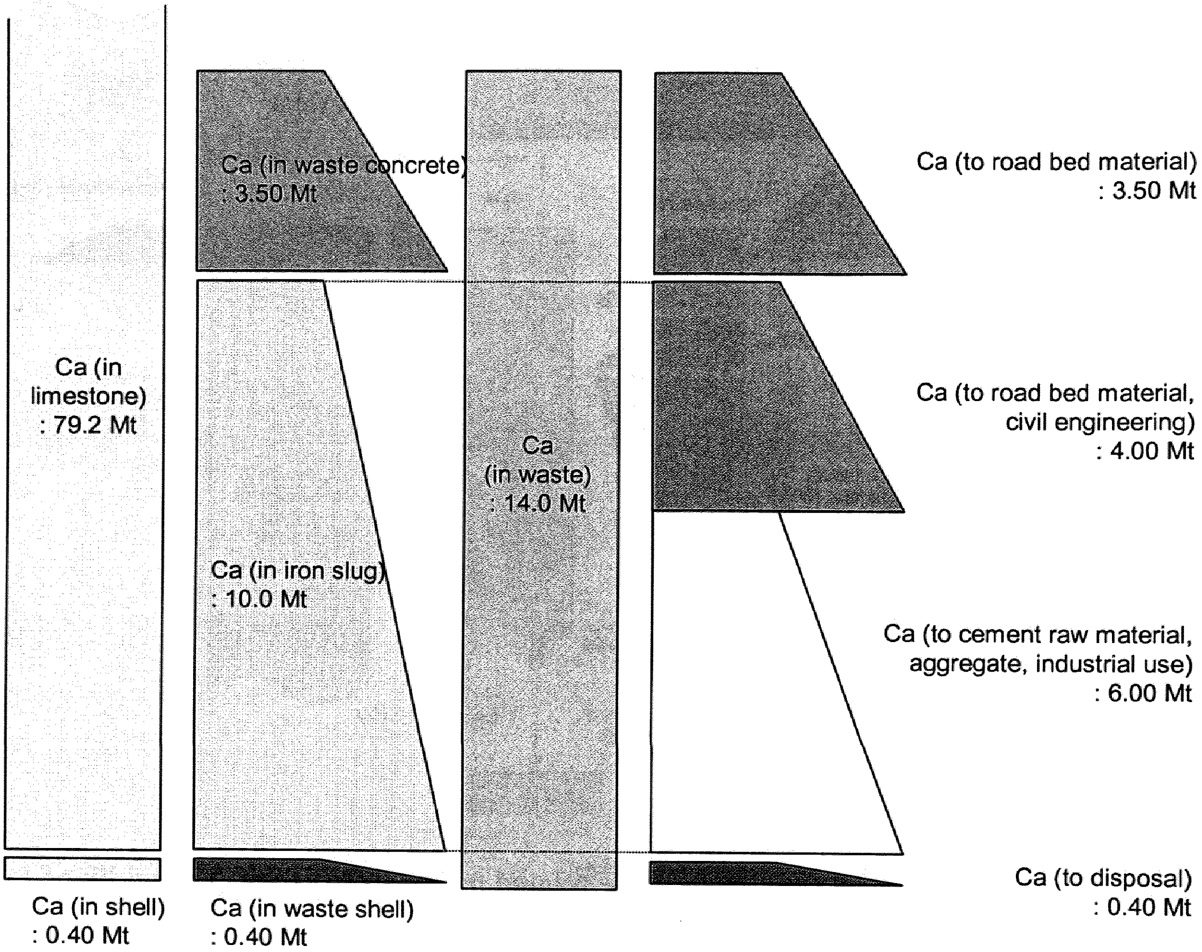

Figure 6.5. Annual material flow of calcium in wastes in Japan. The width of each arrowed line is proportional to its amount.

Table 6.1. Regional data of numbers and CO_2 emissions of steel plants

Area	CO_2 emission [Mt/year]	Steel production [Mt/year]	Number of plant	Basic unit of CO_2 emission
Hokkaido	4.4	2.6	6	1.7 [t-CO_2 / t-steel]
Tohoku	2.5	1.5	5	
Kanto	34.2	20.1	20	
Chubu, Hokuriku	35.7	21.0	14	
Kinki	30.1	17.7	23	
Chugoku	43.6	25.6	10	
Kyusyu	23.5	13.8	6	
Total	178.0	102.0	84	

References: The Japan iron and steel federation, Kobe steel, Nippon keidanren

Table 6.2. Regional data of numbers and CO_2 emissions of cement plants

Area	CO_2 emission [Mt/year]	Cement production [Mt/year]	Number of plant	Basic unit of CO_2 emission
Hokkaido	3.8	5.1	2	0.740 [t-CO_2 / t-cement] (0.440 is derived from limestone pyrolysis)
Tohoku	4.0	5.4	4	
Kanto	6.8	9.2	7	
Chubu, Hokuriku	6.4	8.6	5	
Kinki	4.1	5.5	1	
Chugoku	9.8	13.2	4	
Shikoku	3.7	5.1	2	
Kyusyu	17.5	23.6	9	
Okinawa	0.5	0.7	1	
Total	58.6	76.4	35	

References: The cement shinbun, Japan cement association, Taiheiyo cement, RITE

Table 6.3.a Waste concrete generation, reuse, amount for final disposal in each prefecture in Japan (Hokkaido ~ Mie) (ref. Ministry of Land, Infrastructure and Transport, 2004)

Prefecture Name	Reuse (Kt)		Final disposal (Kt)		Total (Kt)	
Hokkaido (area total)	2,433.3	96.5%	86.6	3.4%	2,519.9	100%
Aomori	544.9	94.5%	31.2	5.4%	576.1	100%
Iwate	412.4	88.3%	54.4	11.6%	466.8	100%
Miyagi	588.4	97.7%	13.8	2.2%	602.2	100%
Akita	389.6	97.2%	11.1	2.7%	400.7	100%
Yamagata	464.1	98.0%	9.4	1.9%	473.5	100%
Fukushima	567.1	98.9%	6.1	1.0%	573.2	100%
Tohoku area total	2,966.5	95.9%	126.0	4.0%	3,092.5	100%
Ibaraki	635.1	99.4%	3.8	0.5%	638.9	100%
Tochigi	476.2	98.6%	6.4	1.3%	482.6	100%
Gunma	622.8	96.2%	24.3	3.7%	647.1	100%
Saitama	814.7	99.7%	1.8	0.2%	816.5	100%
Chiba	1,088.8	99.7%	2.7	0.2%	1,091.5	100%
Tokyo	2,276.0	96.3%	86.9	3.6%	2,362.9	100%
Kanagawa	1,403.1	97.9%	28.8	2.0%	1,431.9	100%
Yamanashi	299.6	96.1%	12.0	3.8%	311.6	100%
Nagano	352.2	96.8%	11.4	3.1%	363.6	100%
Kanto area total	7,968.5	97.8%	178.1	2.1%	8,146.6	100%
Niigata	1,058.5	99.1%	9.5	0.8%	1,068.0	100%
Toyama	548.3	99.7%	1.6	0.2%	549.9	100%
Ishikawa	467.4	98.0%	9.4	1.9%	476.8	100%
Hokuriku area total	2,074.2	99.0%	20.5	0.9%	2,094.7	100%
Gifu	697.5	99.2%	5.4	0.7%	702.9	100%
Shizuoka	1,197.7	99.3%	8.0	0.6%	1,205.7	100%
Aichi	2,096.2	99.8%	4.1	0.1%	2,100.3	100%
Mie	653.9	99.0%	6.1	0.9%	660.0	100%
Chubu area total	4,645.3	99.4%	23.6	0.5%	4,668.9	100%

Table 6.3.b Waste concrete generation, reuse, amount for final disposal in each prefecture in Japan (Fukui ~ Okinawa) (ref. Ministry of Land, Infrastructure and Transport, 2004)

Prefecture Name	Reuse (Kt)		Final disposal (Kt)		Total (Kt)	
Fukui	354.8	99.6%	1.3	0.3%	356.1	100%
Shiga	352.7	99.2%	2.5	0.7%	355.2	100%
Kyoto	567.3	99.5%	2.8	0.4%	570.1	100%
Osaka	1,635.3	97.2%	46.2	2.7%	1,681.5	100%
Hyogo	1,497.8	96.9%	46.5	3.0%	1,544.3	100%
Nara	243.4	95.9%	10.3	4.0%	253.7	100%
Wakayama	302.8	99.3%	1.9	0.6%	304.7	100%
Kinki area total	4,954.1	97.7%	111.5	2.2%	5,065.6	100%
Tottori	216.6	99.5%	0.9	0.4%	217.5	100%
Shimane	356.6	99.3%	2.3	0.6%	358.9	100%
Okayama	451.5	99.5%	2.0	0.4%	453.5	100%
Hiroshima	708.8	95.1%	36.5	4.8%	745.3	100%
Yamaguchi	633.2	98.5%	9.6	1.4%	642.8	100%
Chugoku area total	2,366.7	97.8%	51.3	2.1%	2,418.0	100%
Tokushima	373.1	94.6%	21.2	5.3%	394.3	100%
Kagawa	425.9	96.9%	13.6	3.0%	439.5	100%
Ehime	551.0	96.6%	19.0	3.3%	570.0	100%
Kochi	333.0	88.3%	43.8	11.6%	376.8	100%
Shikoku area total	1,683.0	94.5%	97.6	5.4%	1,780.6	100%
Fukuoka	1,377.0	98.1%	26.5	1.8%	1,403.5	100%
Saga	354.5	97.4%	9.4	2.5%	363.9	100%
Nagasaki	543.6	96.2%	21.3	3.7%	564.9	100%
Kumamoto	462.1	95.6%	20.9	4.3%	483.0	100%
Oita	635.8	96.6%	22.3	3.3%	658.1	100%
Miyazaki	457.2	97.6%	10.9	2.3%	468.1	100%
Kagoshima	911.8	95.0%	47.3	4.9%	959.1	100%
Kyusyu area total	4,742.0	96.7%	158.6	3.2%	4,900.6	100%
Okinawa	414.5	96.2%	16.1	3.7%	430.6	100%
Total	34,248.1	97.5%	869.9	2.4%	35,118.0	100%

Table 6.4. Example cases

		The amount of recycled waste concrete [t/year]		
		30,000	90,000	300,000
Calcium conversion rate to $CaCO_3$ [%]	50	1-a	1-b	1-c
	80	2-a	2-b	2-c

Table 6.5. Lists of material flows and operational conditions for the example cases

	Amount [10^3 t/year/plant]						
	Waste concrete	Waste cement powder	Consumed CO_2	Produced $CaCO_3$	Extracted residue	Waste water	Supplied water
1-a	30	9	0.884	2.01	7.88	4.35	4.35
1-b	90	27	2.65	6.03	23.6	13	13
1-c	300	90	8.84	20.1	78.8	43.5	43.5
Case 1, total [10^3 t/year]	35,000	10,500	1,031	2,345	9,193	5,075	5,075
2-a	30	9	1.41	3.21	7.2	1.84	1.84
2-b	90	27	4.24	9.64	21.6	5.53	5.53
2-c	300	90	14.1	32.1	72	18.4	18.4
Case 2, total [10^3 t/year]	35,000	10,500	1,645	3,745	8,400	2,147	2,147

Table 6.6. Operational conditions for the example cases

Case	Waste cement powder amount [t/year]	Extraction reactor		Reaction conditions						Batch number of times [times/year]
		Volume [m³]	Pressure [MPa]	Temperature [K]	Extraction time [min]		Amount of materials [t/batch]			
					Reaction time [min]	Time for one batch [min]	Waste cement	water	CO_2	
1-a	9,000	5	3	323	5	15	0.1	5	0.006	86,400
1-b	27,000	15	3	323	5	15	0.31	15	0.018	86,400
1-c	90,000	50	3	323	5	15	1.04	50	0.061	86,400
2-a	9,000	4	3	323	10	30	0.21	4	0.01	43,200
2-b	27,000	13	3	323	10	30	0.63	13	0.029	43,200
2-c	90,000	43	3	323	10	30	2.08	43	0.098	43,200

Table 6.7. Capital costs of the recycling plant for the base cases

Case	Capital cost [10^6JPY/plant]		
	Reactors	Others	Total
1-a	30	168	198
1-b	91	362	453
1-c	303	840	1,143
2-a	26	177	203
2-b	77	382	459
2-c	257	887	1,144

Table 6.8. Electricity consumption of the recycling plant for the example cases

Case	Supply electrical power [MW/plant]	Power consumption [GWh/year/plant]
1-a	2.0	14.5
1-b	6.0	43.4
1-c	20.1	144.8
2-a	3.0	21.5
2-b	9.0	64.6
2-c	30.0	215.2

Table 6.9. Breakdown of revenue and costs of the proposed waste concrete recycling plant

No.	Item	Cost [10^6JPY/year]					
		1-a	1-b	1-c	2-a	2-b	2-c
1-	Revenue						
1)	Sale of $CaCO_3$	54.2	162.7	542.4	86.8	260.4	867.9
2)	Sale of extracted residues	0.7	2.1	7.0	0.7	2.1	7.0
2-	Cost						
1)	Employment costs	56.0	56.0	56.0	56.0	56.0	56.0
2)	Material costs	18.0	54.0	180.0	18.0	54.0	180.0
3)	Depreciation cost	16.6	35.8	87.6	17.0	36.2	87.6
4)	Maintenance costs	21.4	47.9	119.5	21.9	48.5	119.6
5)	Utility costs						
-1	Electricity	1.6	4.8	15.9	2.4	7.1	23.7
-2	Water	0.3	0.8	2.6	0.1	0.3	1.1
6)	Wastewater treatment costs	0.9	2.7	8.9	0.4	1.1	3.8
7)	Waste disposal costs	0.0	0.0	0.0	0.0	0.0	0.0
8)	Testing costs	0.0	0.0	0.0	0.0	0.0	0.0
9)	CO_2 capturing costs	19.4	43.0	104.3	27.4	58.1	131.5
	Total	-79.3	-80.2	-25.4	-55.7	1.2	271.6

Table 6.10. Total cost of recycling waste concrete, treatment cost per unit waste cement, and the CO_2 sequestration cost

	1-a	1-b	1-c	2-a	2-b	2-c
Total cost of recycling waste concrete [10^9JPY/35 Mt]	93.4	31.9	3.78	6.58	-0.457	-30.9
Treatment cost per unit waste cement [JPY/t-waste cement]	8893	3040	360.4	6271	-43.5	-2940
The CO_2 sequestration cost [10^3JPY/t-CO_2] ([USD/t-CO_2])	56.8 (498)	19.4 (170)	2.30 (20.2)	63.9 (561)	-0.443 (-3.88)	-29.9 (-262)

Table 6.11. Breakdown of revenue and costs for the proposed waste concrete recycling plant without the process for recrystallization of $CaCO_3$

No.	Item	Cost [10^6JPY/year]					
		1-a	1-b	1-c	2-a	2-b	2-c
1-	Revenue						
1)	Sale of $CaCO_3$	30.1	90.4	301.3	48.2	144.6	482.1
2)	Sale of extracted residues	0.7	2.1	7.0	0.7	2.1	7.0
2-	Cost						
1)	Employment costs	56.0	56.0	56.0	56.0	56.0	56.0
2)	Material costs	18.0	54.0	180.0	18.0	54.0	180.0
3)	Depreciation cost	15.5	32.3	76.2	16.0	33.3	78.0
4)	Maintenance costs	19.9	43.1	103.8	20.6	44.5	106.3
5)	Utility costs						
-1	Electricity	1.5	4.4	14.7	2.3	6.8	22.6
-2	Water	0.3	0.8	2.6	0.1	0.3	1.1
6)	Wastewater treatment costs	0.9	2.7	8.9	0.4	1.1	3.8
7)	Waste disposal costs	0.0	0.0	0.0	0.0	0.0	0.0
8)	Testing costs	0.0	0.0	0.0	0.0	0.0	0.0
9)	CO_2 capturing costs	19.4	43.0	104.3	27.4	58.1	131.5
	Total	-100.6	-143.8	-238.2	-91.9	-107.5	-90.1

Table 6.12. Breakdown of revenue and costs for the proposed waste concrete recycling plant using pure water

No.	Item	Cost [10^6JPY/year]					
		1-a	1-b	1-c	2-a	2-b	2-c
1-	Revenue						
1)	Sale of $CaCO_3$	54.2	162.7	542.4	86.8	260.4	867.9
2)	Sale of extracted residues	0.3	2.1	7.0	0.3	2.1	7.0
2-	Cost						
1)	Employment costs	56.0	56.0	56.0	56.0	56.0	56.0
2)	Material costs	18.0	54.0	180.0	18.0	54.0	180.0
3)	Depreciation cost	16.6	35.8	87.6	17.0	36.2	87.6
4)	Maintenance costs	21.4	47.9	119.5	21.9	48.5	119.6
5)	Utility costs						
-1	Electricity	1.6	4.8	15.9	2.4	7.1	23.7
-2	Water	0.9	2.6	8.7	0.4	1.1	3.7
6)	Wastewater treatment costs	0.9	2.7	8.9	0.4	1.1	3.8
7)	Waste disposal costs	0.0	0.0	0.0	0.0	0.0	0.0
8)	Testing costs	0.0	0.0	0.0	0.0	0.0	0.0
9)	CO_2 capturing costs	19.4	43.0	104.3	27.4	58.1	131.5
	Total	-80.3	-81.8	-31.5	-56.4	0.2	269.0

Table 6.13. Breakdown of revenue and costs for the recycling plant for cases considering the revenue from CO_2 emission reduction

No.	Item	Cost [10^6JPY/year]					
		1-a	1-b	1-c	2-a	2-b	2-c
1-	Revenue						
1)	Sale of $CaCO_3$	54.2	162.7	542.4	86.8	260.4	867.9
2)	Sale of extracted residues	0.3	2.1	7.0	0.3	2.1	7.0
3)	CO_2 emission reduction	9.3	27.8	92.8	14.9	44.6	148.5
2-	Cost						
1)	Employment costs	28.0	28.0	28.0	28.0	28.0	28.0
2)	Material costs	18.0	54.0	180.0	18.0	54.0	180.0
3)	Depreciation cost	16.6	35.8	87.6	17.0	36.2	87.6
4)	Maintenance costs	21.4	47.9	119.5	21.9	48.5	119.6
5)	Utility costs						
-1	Electricity	1.6	4.8	15.9	2.4	7.1	23.7
-2	Water	0.3	0.8	2.6	0.1	0.3	1.1
6)	Wastewater treatment costs	0.9	2.7	8.9	0.4	1.1	3.8
7)	Waste disposal costs	0.0	0.0	0.0	0.0	0.0	0.0
8)	Testing costs	0.0	0.0	0.0	0.0	0.0	0.0
9)	CO_2 capturing costs	19.4	43.0	104.3	27.4	58.1	131.5
	Total	-42.5	-24.1	95.4	-13.3	73.6	448.1

Table 6.14. Environmental impact of the proposed recycling process

Treatment amount of waste concrete	[Mt/year]	35.0
Treatment amount of waste cement	[Mt/year]	10.5
Reduction amount of waste	[Mt/year]	10.5 (35. 0)
Reduction amount of CO_2 emission	[Mt/year]	1.65
Waste water amount	[Mt/year]	2.15
Power consumption	[TWh/year]	25.1
Power supply	[TW]	3.49

7. Conclusions

CONTENTS

7. Conclusions

7. Conclusions

In chapter 1, the situation regarding the generation of waste concrete and the problems related to treatment in Japan were discussed, and the current waste concrete recycling processes overviewed. Based on the situations outlined, the necessity for a new recycling process that enables concrete waste to be recycled, especially "5 mm under" and "hydrated cement particles" was noted.

In chapter 2, a new recycling process for waste concrete utilizing carbonic acid treatment was proposed, and its features were discussed from viewpoints of thermodynamics, kinetics and societal aspects. The proposed process is a technology that will be greatly needed in the near future in Japan, and is considered to be thermodynamically possible. The sociological significance of the proposed process is very large because it makes possible the cyclic use of concrete.

In chapter 3, the technical feasibility of the proposed process was illustrated through lab-scale experiments, and high-purity $CaCO_3$ (calcite type) could be obtained from actual concrete waste. The calcium extraction rate from a waste cement sample and the $CaCO_3$ precipitation rate were measured under various experimental conditions. The purity and particle size of the produced $CaCO_3$ was also measured in this chapter.

In chapter 4, an empirical equation for the "Ca extraction rate from waste concrete" and the "$CaCO_3$ precipitation rate" were deduced based on the experimental results set out in chapter 3.

In chapter 5, process design of the proposed waste concrete recycling plant was conducted to evaluate its economical feasibility. In the process design the current Japanese social situation was taken into account wherever possible, and the data obtained in chapter 3 was used for the process design.

In chapter 6, based on the plant design conducted in chapter 5, the economical feasibility and an environmental impact assessment of the proposed process was conducted for various cases. In the economical feasibility study, the economic impact in the case where the proposed plant is introduced into Japanese society was assessed. As a result, the proposed process is economically feasible in situations where 90,000 metric tons of waste concrete (equivalent to the 0.3 % of the annual waste concrete generation in Japan) is treated in the proposed process. In the environmental impact assessment, the amounts of waste and CO_2 emission reductions, the amount of wastewater and power consumption were considered. The proposed process can reduce CO_2 emission by up to 1.65 Mt in Japan.

Finally, I emphasize the importance of these three points;

- I proposed a novel recycling process for the hydrated cement portion of waste concrete (presently not recycled), and examined the technical feasibility of the process.
- I deduced the empirical equations for the "Ca extraction rate from waste concrete" and the "$CaCO_3$ precipitation rate" from experiments, and obtained data in respect to purity and particle size of the $CaCO_3$ produced.
- I examined the economical feasibility of the proposed waste concrete recycling process through process design.

Published articles

1. Yasuro Katsuyama, Akihiro Yamasaki, Atsushi Iizuka, Minoru Fujii, Kazukiyo Kumagai, and Yukio Yanagisawa, Development of a process for producing high-purity calcium carbonate ($CaCO_3$) from waste cement using pressurized CO_2, *Environmental Progress*, **24** (2), pp.162 - 170, 2005.

2. Atsushi Iizuka, Minoru Fujii, Akihiro Yamasaki, and Yukio Yanagisawa, Development of a New CO_2 Sequestration Process Utilizing the Carbonation of Waste Cement, *Industrial Engineering & Chemistry Research*, **43** (24), pp.7880 - 7887, 2004.

Development of a New CO_2 Sequestration Process Utilizing the Carbonation of Waste Cement

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We propose a new sequestration process for anthropogenic carbon dioxide (CO_2) that uses waste cement. The proposed process consists of two main reactions. The first is the extraction of calcium ions (Ca^{2+}) from waste cement particles by pressurized carbon dioxide (several megapascals of pressure). The second is the precipitation of calcium carbonate ($CaCO_3$). Ca^{2+} extracted from waste cement is deposited as $CaCO_3$ when the pressure is reduced. $CaCO_3$ is disposed of directly, or recycled as a raw material for cement production. In the latter case, the same amount of CO_2 is considered to be sequestered because the net amount of virgin limestone mined can be reduced. The power consumption and cost of the proposed sequestration process for CO_2 emitted from a 100 MW thermal power plant were evaluated, on the basis of laboratory-scale experimental results. The power consumption for the operating process strongly depended on the operating conditions such as the cement/water ratio, the CO_2 pressure, and the average cement diameter. The minimum power consumption was 25.9 MW/100 MW of power generation when optimized within the operating conditions studied experimentally, and the sequestration cost associated with the power consumption (excluding capital and maintenance) would be about $22.6/t of carbon dioxide. This result indicates that the present process is highly competitive with previously reported CO_2 sequestration scenarios such as ocean sequestration. Sensitivity analysis of the operating parameters was carried out on the operating power consumption, and it was found that a smaller ratio of waste cement to water and a lower CO_2 pressure will decrease the operating power consumption.

1. Introduction

A variety of carbon dioxide (CO_2) sequestration scenarios have been proposed as options for mitigating global warming, including ocean disposal and underground sequestration. In these scenarios, CO_2 is directly discharged to the sequestration sites, i.e., deep sea or underground, and is sequestered there in the form of liquid CO_2 or dissolved in the water. CO_2 sequestered in such forms could cause severe damage to the environment, by reducing the pH of the ambient seawater, or by abrupt evaporation to the surface.

Sequestration of CO_2 in the form of calcium or magnesium carbonates could realize more environmentally benign scenarios, because these compounds are extremely stable in the environment. The implementation of CO_2 sequestration in the form of carbonates, however, requires a tremendous amount of calcium or magnesium to handle the continuous effluent of anthropogenic CO_2. Natural rocks containing calcium or magnesium such as serpentine[1,2] or wollastonite[3] have been tested as alkaline-earth-metal sources for carbonate formation. Although thermodynamic calculations indicate that carbonate formation reactions can proceed spontaneously, the reaction rates observed when these sources were reacted with CO_2 under rather mild conditions were extremely slow. Thus, an appropriate acceleration method is needed to make carbonate formation a practical method for CO_2 sequestration. Several acceleration methods have been examined so far, including increasing the surface area of rock particles by pulverization,[4] use of acceleration media such as hydrochloric acid[5] or acetic acid,[3] dissolved forms of carbonate compounds such as calcium hydrogen carbonates,[6,7] and iron carbonates,[8] and application of high temperature and pressure conditions, where CO_2 is in the supercritical state.[1,2] Although considerable acceleration of the reaction rates was realized by these methods, they may require more power consumption, or treatment of waste acids. In this paper, we propose a new method for CO_2 sequestration, using waste cement as a calcium source for carbonate formation.

Waste cement is a calcium-rich waste product containing calcium in the form of calcium silicate hydrate (for example, $3CaO{\cdot}2SiO_2{\cdot}3H_2O$) and calcium hydroxide ($Ca(OH)_2$). Waste cement is produced in the process that recovers aggregates from waste concrete. While recycling and reuse of the recovered aggregates is an established process, reuse of waste cement has been limited to use as a roadbed material, and no effective utilization has yet been realized. Because of a continuous increase in the supply of waste concrete from dismantled buildings, a long-term copious and stable supply of waste cement is expected in the future. Thus, waste cement is considered to be a potential calcium source for the formation of carbonate for CO_2 sequestra-

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tion, which will be available on the scale required for CO_2 sequestration. In addition, the carbonation product from waste cement, calcium carbonate ($CaCO_3$), can be reused as a raw material in cement manufacturing. In that case, the carbonation process can be regarded as a cement recycling process. In such a recycling process, the CO_2 emission in the cement production process can be reduced by the amount of CO_2 that would potentially be emitted from virgin limestone. Since the calcium components in the waste cement are more reactive than those in calcium-containing rocks, more effective carbonation processes would be anticipated in terms of the reaction rate. The expected reaction scheme with CO_2 is as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{1}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{3}$$

$$3CaO{\cdot}2SiO_2{\cdot}3H_2O + 6H^+ \rightarrow 3Ca^{2+} + 2SiO_2 + 6H_2O \tag{4}$$

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \tag{5}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow \tag{6}$$

Reactions 1–3 represent the dissociation of dissolved CO_2 in water, reactions 4 and 5 represent the extraction of calcium ions from waste cement with carbonic acid, and reaction 6 represents the precipitation of calcium carbonate. The above reaction scheme shows a process that proceeds spontaneously, without requiring the addition of heat to react. However, to examine the feasibility of the process, reaction rate data are necessary, and should be determined experimentally under various conditions.

In a previous paper,[9] we proposed a new concept for CO_2 sequestration by using a waste cement stream, and demonstrated the feasibility of this process with preliminary experimental results. In this study, a new experimental apparatus was designed and more comprehensive data, e.g., data investigating influences of the waste cement/water ratio, partial pressure of CO_2, and particle size of the waste cement on the extraction rate of the calcium ions, were obtained. Significant improvements in the extraction performance of calcium ions from the waste cement were observed. On the basis of the newly obtained results, process feasibility was examined for a wider range of operating conditions, and process optimization in terms of power consumption was conducted.

2. Outline of the Proposed Process

An outline of the proposed process is illustrated schematically in Figure 1. Waste concrete discharged from dismantled buildings is first pulverized and classified into aggregates and waste cement particles. The waste cement particles, which have a mean diameter of about 100 μm, are fed into a high-pressure reactor vessel to extract calcium ions with pressurized CO_2 and water. The CO_2 is captured and separated from concentrated emission sources such as thermal power plants. In the extraction vessel, the extraction of calcium ions from waste cement (reactions 4 and 5) would take place with stirring. Due to the high solubility of $CaCO_3$ under high-pressure CO_2 conditions, the extraction reactions will proceed in the extraction vessel. After a certain period of time, the slurry is filtered and the solution phase is separated. Then, the solution is left under low-pressure CO_2 conditions in the settling bath to allow precipitation of $CaCO_3$ to take place. The $CaCO_3$ product can be either used as a raw material in the cement production industry or disposed of in appropriate sites. In the former case, the proposed process could be regarded as recycling waste concrete, while the latter case could be regarded as a CO_2 sequestration process.

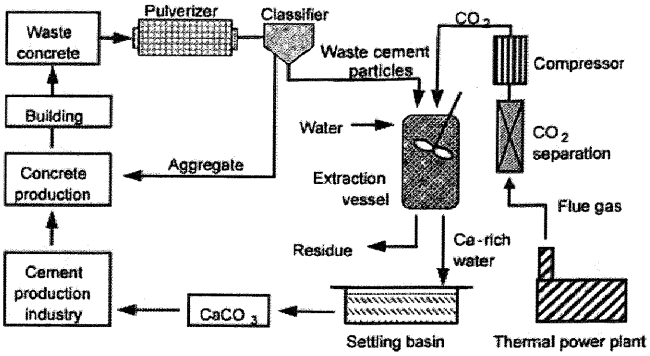

Figure 1. Schematic drawing of the CO_2 sequestration process.

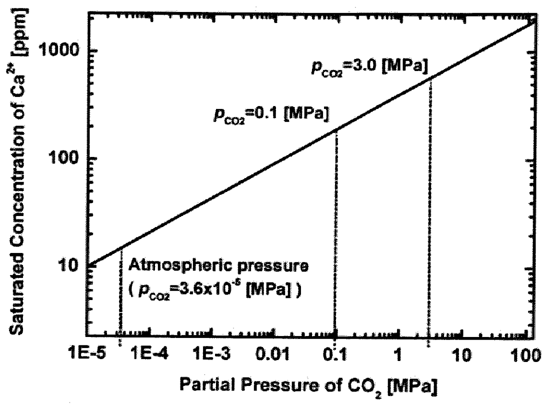

Figure 2. Equilibrium concentration of calcium ions in a water–CO_2–Ca^{2+} system as a function of CO_2 pressure (temperature 323 K).

3. Thermodynamic Considerations

From a thermodynamic point of view, the maximum conversion of calcium content in the waste cement to $CaCO_3$ depends on two factors, the solubility of calcium ions in the extraction process and the solubility of calcium ions in the precipitation process. The net production of $CaCO_3$ depends on the difference in solubility between the extraction process and the precipitation process. Figure 2 shows the results of the thermodynamic calculations on the CO_2 pressure dependence of the solubility of calcium ions at 323 K. The equilibrium constants were obtained from the literature.[10,11] The solubility strongly depends on the CO_2 pressure; the solubility of calcium ions at $p_{CO_2} = 3.0$ MPa is 3 times that at $p_{CO_2} = 0.1$ MPa. Thus, the maximum conversion to $CaCO_3$ is more than 67% when the extraction is conducted at 3.0 MPa and the precipitation at 0.1 MPa. If the precipitation process is conducted

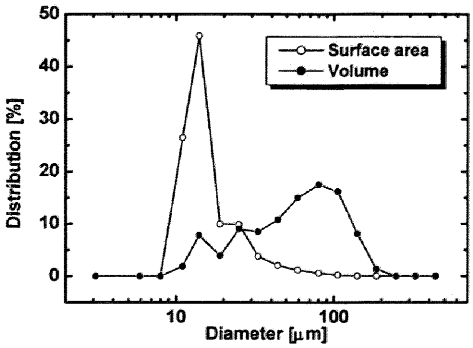

Figure 3. Particle size distributions of waste cement particles measured by laser light scattering.

under atmospheric conditions (p_{CO_2} = 36 Pa), the maximum conversion is about 96%.

4. Experimental Section

Although the thermodynamic calculations indicate that it is theoretically possible to convert more than 67% of the calcium content in the waste cement into calcium carbonate, the practical conversion rate would largely be determined by the reaction kinetic factors. The kinetic data for the extraction process should be determined for the design of both the extraction and precipitation processes. In this study, only extraction kinetics are considered, because dependence of the rate of the extraction reaction on the extraction conditions is critical for the process design and the process power consumption, while the precipitation reaction will be conducted under low-pressure conditions without power consumption.

4.1. Characterization of the Waste Cement Sample. The waste cement sample used in this study was kindly supplied by Tateishi Construction Corp. The sample is of fine particles obtained as a byproduct in a recycling plant for waste concrete. The sample was characterized by measuring the particle size distribution, elemental analysis, and measurement of the degree of carbonation.

Figure 3 shows the size distribution of sample particles, measured by a laser-scattering particle size measurement apparatus (Shimadzu, SALD1100). The horizontal axis denotes the light-scattering diameter (μm). The diameter of the waste cement particles was distributed over the range of 10−200 μm, with a peak at about 25−40 μm (area-based) or about 80 μm (volume-based).

The elemental composition was analyzed by X-ray fluorescence (JEOL, JSX-3220). The weight fraction of calcium was determined to be about 27.3% of the waste cement.

Carbonation of the waste cement will reduce the potential capacity for CO_2 sequestration. Since the waste cement originated from dismantled buildings several decades old, the calcium content would have been exposed to carbonation by atmospheric CO_2 for a long period of time. The carbonation kinetics of cement in concrete have been studied by several authors, and the degree of carbonation is normally limited to within several millimeters of thickness from the surface for about 3 years.[12] It is generally realized that the depth of carbonation is proportional to the square root of the exposure time; after 50 years of exposure, the neutralization depth of concrete is still limited to about 1 cm from the surface. Considering the thickness of concrete used in buildings, the carbonation is limited to near the surface exposed to the atmosphere. The degree of carbonation of the samples was determined by a thermogravimetric method with a differential thermal analyzer (ULVAC, TGD-9600). It was found that about 11% of the total calcium in the waste cement was already carbonated. Therefore, 0.27 t of CO_2 (= 1 × 0.273 × 0.89 × 44/40) can be sequestered when 1 t of the waste cement is completely carbonated. This number is an underestimated value because the degree of carbonation in a normal situation is much lower than 11%.

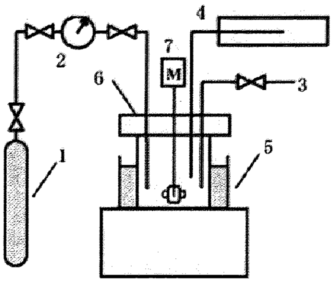

Figure 4. Schematic drawing of the experimental apparatus for calcium extraction: (1) CO_2 cylinder, (2) pressure gauge, (3) sampling line, (4) temperature gauge, (5) water bath, (6) reactor, (7) stirrer.

4.2. Calcium Extraction Experiments. 4.2.1. Experimental Apparatus and Identification of the Extracted Particles. Calcium extraction experiments on the waste cement were conducted by using a batch-type stirring vessel with a 500 mL inner volume. A schematic diagram of the experimental apparatus is shown in Figure 4. A given amount of the waste cement particles was fed with water into the stirring vessel under atmospheric conditions. Then, gaseous CO_2 was supplied to the vessel until the pressure of the vessel reached the experimental pressure. The extraction vessel was immersed in a constant-temperature bath, the temperature of which was controlled with an accuracy of ±1 °C. The CO_2 pressure in the vessel was controlled by a back-pressure-controlling valve installed at the downstream side of the extraction reactor. The slurry contents in the vessel were stirred using a two-wing paddle-type fin which can be altered to stir at rates in the range of 0−1000 rpm. During the extraction experiments, the vessel contents were sampled at given intervals through a sintered-metal filter with 5 μm mesh. The filtered solution was then depressurized to atmospheric pressure, and the concentration of calcium ions was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; Hitachi, P-4010). The extraction ratio and rate were determined from the change in the concentration of calcium ions over time in the sample solution.

The extraction rate may depend on a variety of conditions. In this study, the influences of the following parameters were investigated experimentally: initial weight ratio of waste cement to water, partial pressure of CO_2, and size distribution of the waste cement.

Analysis of the composition of the waste cement extract was carried out on the particles remaining after evaporation of water from the sampled solution, using X-ray diffraction analysis (Rigaku, Mini Flex) and X-ray fluorescence analysis (JEOL, JSX-3220). The X-ray diffraction pattern of the particles remaining after evaporation of water from the sampled solution was similar to that of calcite. X-ray fluorescence analysis

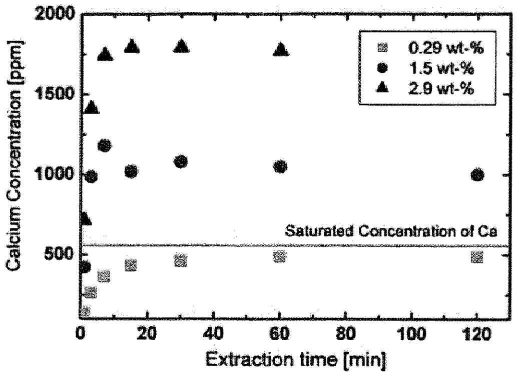

Figure 5. Change in concentration of calcium ions for various initial amounts of waste cement particles. Other operating conditions: temperature 323 K, stirring rate 900 rpm, CO_2 pressure 3.0 MPa, average particle diameter of the waste cement 10–200 μm. The dotted line shows the saturated concentration of calcium under the extraction conditions used.

demonstrated that the calcium fraction of the metal content in the remaining particles was larger than 97%. These results show that high-purity $CaCO_3$ (calcite) can be obtained from the waste cement particles by the extraction procedures used in these experiments.

4.2.2. Influence of the Initial Ratio of Waste Cement to Water on the Extraction Rate. Figure 5 shows the time course of the calcium concentration in the sample solution filtered from the reactor for various initial amounts of 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 in the range of 0.29–2.9 wt %. Other experimental conditions were constant for all the runs: stirring rate 900 rpm, temperature 323 K, $p_{CO_2} = 3.0$ MPa.

The calcium concentration increased almost linearly with increases in the reaction time, up to about 10 min, for all the cases. After that, the concentration leveled off or decreased slightly. The initial rate of increase of the calcium concentration increased with an increase in the initial amount of waste cement. The dotted line in Figure 5 represents the saturation concentration of calcium ions obtained by the thermodynamic calculations. The sampled solution was supersaturated with calcium ions even at the early stage of the extraction reaction, except in the case with the smallest ratio of waste cement to water (0.29 wt %). A higher degree of supersaturation was observed with a larger initial amount of waste cement. Supersaturation occurred because the deposition rate of calcium carbonate from the solution was much slower than the extraction rate of calcium ions from the waste cement. At the later stage of the reaction, however, the deposition only occurs gradually, its rate is balanced by the extraction rate, which may be reduced by decreasing the amount of calcium source in the waste cement, and a leveling off of the calcium concentration in the solution phase occurs. Alternatively, the deposition rate could exceed the extraction rate if the amount of calcium source in the waste cement were decreased, and the concentration would then drop to reach the equilibrium solubility. For the case of a small ratio of waste cement to water, the extraction rate would be balanced by the deposition rate at an earlier stage of the reaction experiment, and the concentration of calcium ions would not exceed that given by the solubility line.

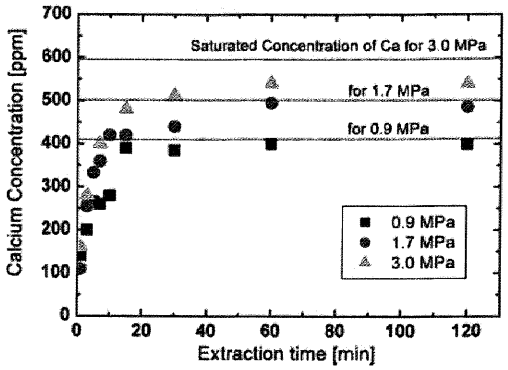

Figure 6. Change in concentration of calcium ions at various partial pressures of gaseous CO_2. Other operating conditions: temperature 323 K, stirring rate 900 rpm, ratio of waste cement to water 0.29 wt %, average particle diameter of the waste cement 10–200 μm. The dotted lines show the saturated concentration of calcium under each extraction condition.

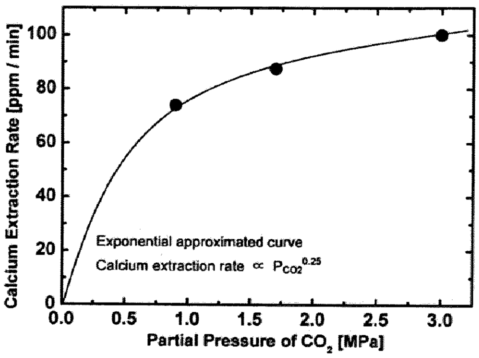

Figure 7. Calcium extraction rate during the initial stage of the reaction (until 3 min for all runs) as a function of the partial pressure of CO_2.

The extraction ratio of calcium (equal to calcium concentration × solution volume/total calcium amount in the waste cement × 100) after 7 min of extraction was about 50% for the run with the smallest ratio of waste cement to water (0.29 wt %) and 22% for the run with the largest ratio (2.9 wt %). Thus, a large portion of the calcium content of waste cement is available if there is enough water. When there was an abundance of waste cement, the high calcium extraction rate that caused the supersaturation state was observed. Thus, the proposed process has the potential to simultaneously achieve a rapid extraction rate and a high calcium utilization ratio as a result of any improvements to the contact method between waste cement and water.

4.2.3. Influence of CO_2 Pressure. Figure 6 shows the influence of the CO_2 pressure on the time course of the concentration of calcium ions in the solution phase. The experimental conditions were stirring rate 900 rpm, temperature 323 K, and initial amount of waste cement 1.0 g in 350 g of water (the waste cement to water ratio equals 0.29 wt %). Similar trends were observed for all the runs, with the concentration increasing quickly during the initial stage of the reaction, and then leveling off. The rate of increase in the calcium concentration during the initial stage of the reaction was found to increase with an increase in the CO_2 pressure. The increase in the initial extraction rate with increasing CO_2 pressure could be attributed to the increase in the solubility of calcium ions. With an increase in the solubility, the driving force of the extraction reaction would increase and result in the increased extraction rate. Figure 7 shows the initial (until 3 min) extraction reaction rate change as a function of the partial pressure of CO_2. The initial extraction rates were approximately

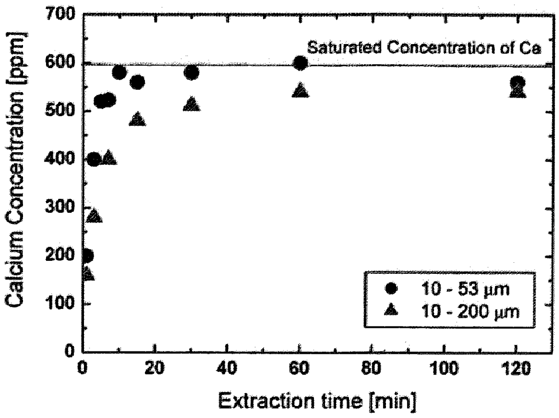

Figure 8. Change in concentration of calcium ions for different diameters of waste cement. Other operating conditions: temperature 323 K, stirring rate 900 rpm, initial ratio of waste cement to water 0.29 wt %, CO_2 pressure 3.0 MPa.

proportional to about a quarter power of the partial pressure of CO_2.

4.2.4. Influence of the Particle Size of the Waste Cement. Figure 8 shows the time course of the calcium concentration in the solution phase for waste cement with different particle size distributions. The sample with smaller sized particles was prepared by filtering the raw waste cement particles through a mesh of 53 μm, and the sample with larger sized particles was raw waste cement. The figure indicates that the initial rate of extraction was higher for the sample with smaller particles than for that with larger particles. Since the initial amounts of waste cement in these two samples are equal, the larger specific surface area of the smaller particles would account for the higher extraction rates. Therefore, pulverization of the waste cement particles would increase the initial extraction rate by increasing the effective surface area.

In summary, the experimental study demonstrated that the extraction of calcium ions from waste cement particles proceeds at relatively high rates, and about 30% of the calcium could be extracted under typical conditions. Therefore, the proposed process could be useful in terms of the extraction reaction. However, to examine the feasibility of the process, quantitative analysis of the process design in terms of power consumption and cost is necessary.

5. Process Design and Evaluation

On the basis of the experimental results, a CO_2 treatment process was designed and the power consumption for the operation was estimated, focusing on the extraction step. In addition, the effects of extraction conditions such as CO_2 pressure, initial ratio of waste cement to water, and size of the waste cement particles on the process power 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/yr.[13] Since the weight fraction of active calcium in the present waste cement sample is about 24.3%, 2.26×10^6 t/yr of waste cement would be necessary to treat the total amount of CO_2 emitted from the power plant, assuming 100% conversion. Generally, cement is mixed with about 55 wt % water when it is used to form concrete. Thus, 2.26×10^6 t/yr of waste cement is equivalent to 1.46×10^6 t/yr of cement (waste cement consists of water and cement). Considering the total amount of waste cement produced in Japan (1.23×10^8 t/yr in 2001) being used for the present process, the potential capacity of the CO_2 treatment is about 3.00×10^7 t/yr. This amount is about 10% of the annual emission of CO_2 from the electric power generation sector (3.12×10^8 t/yr).[14]

It is assumed that the waste cement is supplied in particle form, with a mean diameter of about 5 cm, from building demolition. The waste cement particles should be pulverized to smaller particles to enhance the extraction efficiency. Bond's equation[15] was applied to estimate the energy required for pulverization. In this study, it is assumed that the waste cement particles are pulverized from 5 cm to less than 200 μm. We used the value for cement raw material as the constant of proportion for Bond's equation.

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 flue gas will be conducted by a liquid absorption process with monoethanolamine. To enhance the extraction efficiency, CO_2 will be pressurized from 0.1 MPa to the reaction pressure (for example, 3.0 MPa) and heated from room temperature to the reaction temperature. The CO_2 will be pressurized before introduction to the extraction reactor, by adiabatic compression with 90% efficiency.

The reactor volume required was determined from the CO_2 emission rate and the retention time in the extraction reactor. The retention time is assumed to be 3.0 min. 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 relative to those of the extraction vessel used in the experiments. Only the 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 the reactant up to the extraction temperature.

After extraction, the solution phase and the remaining particles of waste cement will be separated by sedimentation in a settling basin. The solution phase will be depressurized to atmospheric pressure for calcium carbonate particle deposition. The calcium carbonate particles will then be disposed of in an appropriate site, or recycled to the cement manufacturing industry. The energy requirement for these processes would be negligible compared with those for the preceding extraction and pretreatment processes.

Figures 9–11 show the dependence of the power consumption and its breakdown on the operating conditions, the ratio of waste cement to water (Figure 9), CO_2 pressure (Figure 10), and size of the waste cement (Figure 11), with the other conditions being fixed. In all cases, the pressurization process after capturing CO_2 will consume the largest amount of energy, which determines the order of the total power consumption among the extraction options. Figure 9 shows that the power consumption required for CO_2 pressurization decreases with an increase of the ratio of waste cement to water. The portion of CO_2 utilized for the carbonate production will be increased when the ratio of waste cement to water is increased, where a supersaturation

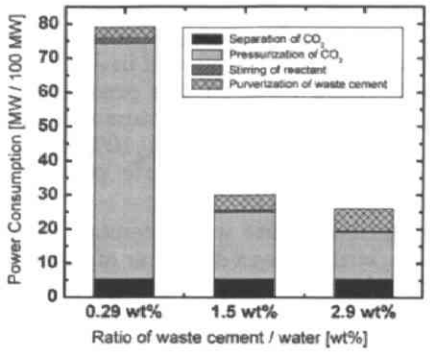

Figure 9. Breakdown of the power consumption of operating the CO_2 treatment process. Influence of the initial ratio of waste cement to water on the power consumption. Other operating conditions: CO_2 pressure 3.0 MPa, average particle diameter of the waste cement 10−200 μm.

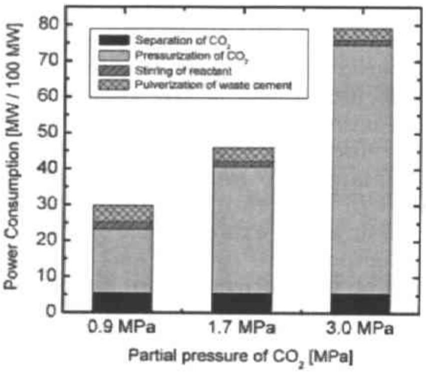

Figure 10. Breakdown of the power consumption of operating the CO_2 treatment process. Influence of the initial CO_2 pressure on the power consumption. Other operating conditions: ratio of waste cement to water 0.29 wt %, average particle diameter of the waste cement 10−200 μm.

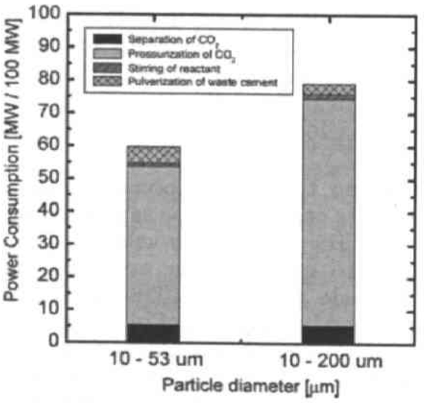

Figure 11. Breakdown of the power consumption of operating the CO_2 treatment process. Influence of the average particle diameter of the waste cement powder on the power consumption. Other operating conditions: initial ratio of waste cement to water 0.29 wt %, CO_2 pressure 3.0 MPa.

condition is realized. As a result, the amount of CO_2 to be pressurized for extracting a given amount of calcium ions (equal to the amount of CO_2 to be fixed as $CaCO_3$) will be decreased. Thus, the energy required for operating the process (mainly pressurization of CO_2) will be decreased with increasing ratio of waste cement to water. The power consumption could be reduced by decreasing the CO_2 pressure supplied for the extraction process as shown in Figure 10. In the water−CO_2−Ca^{2+} system, the ratio of Ca^{2+} to dissolved total CO_2 increases with a decrease in the partial pressure of gaseous CO_2

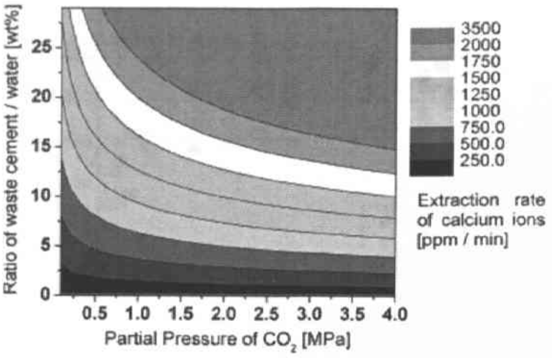

Figure 12. Contour plot of the estimated extraction rates of calcium ions from waste cement as a function of the initial ratio of waste cement to water and the partial pressure of CO_2. The average particle diameter of the waste cement is fixed at 10−200 μm.

fed into the system. Because of this effect, the lower CO_2 pressure condition leads to an increase in the ratio of CO_2 utilized for the calcium extraction, and the power consumption for pressurizing CO_2 is decreased. Figure 11 shows that the reduction of the particle size of the waste cement by pulverization will decrease the total power consumption. A higher extraction rate of calcium ions can be realized for smaller particles of waste cement due to the larger specific surface area available for the extraction reaction. As a result, the amount of CO_2 necessary to extract a given amount of calcium will be decreased, and the power consumption will be reduced albeit there is a greater power consumption for the pulverization of waste cement.

Thus, the power consumption and the cost are strongly dependent on the operating conditions such as the initial ratio of the waste cement to water, the partial pressure of CO_2, and the size of the waste cement. The total power consumption increased 3-fold when the initial amount of waste cement/water was decreased from 2.9 to 0.29 wt %. The operation under lower pressure conditions would also significantly decrease the power consumption. The minimum power consumption among the cases studied was 25.9 MW, for the case with an initial ratio of waste cement to water of 2.9 wt % (10 g/350 mL), $p_{CO_2} = 3.0$ MPa, and a temperature of 323 K. Under these conditions, the energy and cost for the CO_2 sequestration were calculated to be about 420 (kW h)/t of CO_2 (equivalent to 25.9 MW/100 MW of power generation) and $22.6/t of CO_2, respectively. The cost for the CO_2 sequestration was calculated from the power consumption, on the basis of the price of electricity (about $0.1/(kW h)). It was assumed that there would be a profit from selling the $CaCO_3$, and this was included in the cost calculation. Table 1 shows the breakdown of the power consumption for each sector. This power consumption is comparable to that of the ocean sequestration options,[13] and the cost is much smaller, due to the profit from selling the $CaCO_3$. There should be room for improvement, by further optimization of the operating conditions for the extraction, especially the extraction pressure, where almost half of the energy is consumed by the pressurization of the feed CO_2 gas. Note only the cost associated with the power consumption for operating the process is considered in the above estimations and evaluations. The COM costs, namely, the plant construction cost (capital cost), non-energy operation cost such as labor cost, and maintenance cost, were excluded from the estimation. The real cost would be somewhat more expensive than the

Table 1. Breakdown of the Estimated Power Consumption and Operating Cost of the Proposed Treatment Process of CO_2 under an Optimized Extraction Condition[a]

	CO_2 separation	pressurization	stirring	pulverization	revenue by selling $CaCO_3$	total
power consumption per 100 MW of power generation (MW/100 MW)	5.5	13.7	0.32	6.4		25.9
power consumption for CO_2 treatment [(kW h)/t of CO_2]	89	223	5	104		421
operating cost for CO_2 treatment tind($/t of CO_2)	7.9	19.9	0.55	9.3	15.0	22.6

[a] The ratio of the calcium in the waste cement utilized for the CO_2 treatment is 18.1%.

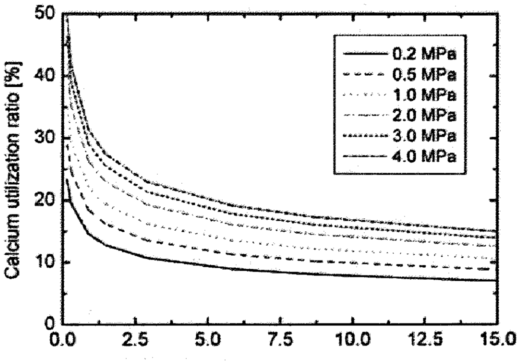

Figure 13. Ratio of calcium in the waste cement utilized for the CO_2 treatment process as a function of the initial ratio of waste cement to water and the partial pressure of CO_2. The average particle diameter of the waste cement is fixed at 10−200 μm.

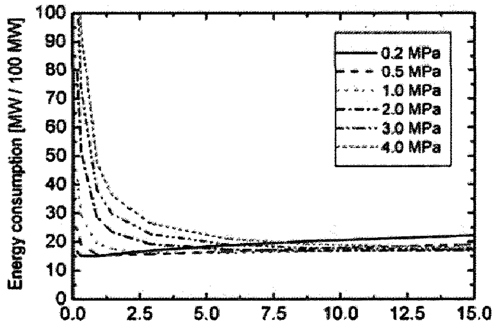

Figure 14. Dependence of the power consumption of operating the CO_2 treatment process as a function of the initial ratio of waste cement to water and the partial pressure of CO_2. The average particle diameter of the waste cement is fixed at 10−200 μm.

estimated values when the COM costs are included: the COM costs are in general about 5% of the direct operating cost for the process.

The above results were limited to the operating conditions that corresponded to the laboratory experiments conducted in this study. To obtain a greater insight into the effects of the operating conditions and search for more feasible ones, estimates of the power consumption of the proposed process were carried out for a wider range of conditions, by extrapolation of the experimental extraction data. The experimental results demonstrated that the initial (until 3.0 min) extraction rates were approximately proportional to the 0.25 power of the partial pressure of CO_2, and were proportional to the 0.74 power of the initial ratio of waste cement to water. On the basis of this extrapolation, the influences of CO_2 pressure and initial ratio of waste cement to water on the process power consumption were simulated. Figure 12 shows the calcium extraction rate as a function of the partial pressure of gaseous CO_2 and the ratio of waste cement to water. The rate of calcium extraction from waste cement increases with increases in the partial pressure and the ratio of waste cement to water. On the other hand, as shown in Figure 13, the percentage of calcium utilized for the extraction decreased with increases in the CO_2 pressure and initial ratio of waste cement to water. For the given extraction rate, the same process design as discussed previously was applied. Figure 14 shows the results of the power consumption estimates for carbon dioxide sequestration as a function of the ratio of waste cement to water and the partial pressure of CO_2. In the case with a high partial pressure of CO_2 and a low ratio of waste cement to water, the power consumption is very large. Furthermore, in the case with a high ratio of waste cement to water, the power consumption is also large. The ratio of waste cement to water has a more significant influence on the power consumption than the partial pressure of CO_2. According to the simulation, the optimized operating conditions of the sequestration plant have a lower partial pressure of CO_2 and a higher ratio of waste cement to water than those we studied, and the process is highly competitive with existing sequestration methods such as ocean sequestration. However, the problem of a low calcium utilization ratio remains. A high calcium extraction rate from waste cement into water is easily obtained by enhancing the ratio of waste cement to water (Figure 12), but the calcium utilization ratio often decreases under such conditions (Figure 13). A method to increase the calcium utilization ratio is needed to successfully implement the proposed process.

6. Conclusions

Through the experiments and evaluations reported here, it was confirmed that the extraction rate of calcium ions from waste cement particles is high enough to be of use in the proposed process. Sequestration of anthropogenic CO_2 by the proposed process was considered technically possible. The minimum power consumption for the direct operation of the present process to sequester CO_2 emitted from a 100 MW thermal power plant was estimated to be 420 (kW h)/t of CO_2, and the operating cost associated with the power consumption was about \$22.6/t of CO_2 for an optimized operation condition within the range experimentally studied. Although the capital, operating (nonpower), and maintenance costs were not included in the estimation, this above estimated cost is comparable with those of ocean sequestration scenarios, indicating that the proposed process for CO_2 sequestration is a feasible option. A method to increase the calcium utilization ratio is needed to successfully implement the proposed process. Sensitivity analysis of the operating conditions such as the ratio of waste cement to water, CO_2 pressure, and particle size of the waste cement was carried out on the operating power consumption. The smaller ratio of waste cement to water and the lower CO_2 pressure will reduce the operating power consumption, although the ratio of calcium in the waste cement utilized for the sequestration will be reduced.

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Development of a Process for Producing High-Purity Calcium Carbonate ($CaCO_3$) from Waste Cement Using Pressurized CO_2

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A new type of process for producing high-purity calcium carbonate from waste cement powder was developed. The process consists of two main reactions; extraction of calcium in the form of calcium ions from waste cement powder in a water slurry by pressurized CO_2 *(typically at several MPa), and precipitation of calcium carbonate* ($CaCO_3$) *from the extracted solution by reduction of the* CO_2 *pressure. The process can be recognized as the emission reduction process of* CO_2 *as well. Laboratory-scale experimental studies were conducted for both the extraction reaction and the precipitation reaction, to examine the feasibility of the process. The extraction process was found to proceed at a relatively high rate, especially during the initial 10 min. The concentration of calcium ions exceeded the thermodynamic solubility of* $CaCO_3$ *(supersaturation) when abundant waste cement was available. After filtration of the residues,* $CaCO_3$ *particles with >98% purity were obtained by depressurizing the* CO_2*. The dependency of the reaction rates on the operating conditions, such as the ratio of waste cement to water,* CO_2 *pressure, and particle size of waste cement particles, was investigated. A process design was carried out based on the experimental results, assuming that the present process is applied to two types of* $CaCO_3$ *production process: flue gas desulfurization and production of ultrahigh-purity* $CaCO_3$*. The estimated costs per 1 metric ton of* $CaCO_3$ *were USD 136 for desulfurization and USD 323 for high-purity* $CaCO_3$*.* © 2005 American Institute of Chemical Engineers Environ Prog, 24: 162–170, 2005

INTRODUCTION

Portland cement is widely used as a building material in the form of concrete mixed with water, aggregates, and some additives such as clay. In concrete, the cement component exists in the form of alkaline compounds such as calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 3H_2O$) 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 (such as carbonic acid). Concrete buildings are dismantled at the end of their lifetime, and the waste concrete generated is one of the main construction wastes. 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 [1]. It is predicted that a huge number of concrete

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buildings built in the high-growth period of the 1960s and 1970s will have to be demolished in the next 10 to 20 years, thus generating a tremendous amount of waste concrete. Establishment of processes that can recycle or reuse waste concrete is thus an urgent and important issue.

Processes to recover aggregates from waste concrete have been proposed: the aggregates in the waste concrete are recovered by pulverization and classification of the waste concrete. Waste cement powder is a by-product of such aggregate recycling processes. Because the weight fraction of the waste cement is as high as about 1/3 of the total waste concrete, it is necessary to establish an effective treatment process of the waste cement. At the present, most of the waste cement has been either used as roadbed material or simply disposed of. Several efforts have been made to reuse waste cement as a raw material for cement production [2, 3]. However, the hydraulic or caking properties of the reproduced cement from the waste cement were not sufficiently high to be reused as a building material. Production processes of other building materials, such as tobermorite [4, 5] or hard material by mixing with glass [6] from waste cement, have been investigated. On the other hand, waste cement is used as a source of CO_2 sequestration; CO_2 sequestration processes have been carried out with the artificial weathering reaction of rocks such as wollastonite, serpentine, and so on [7–12]. Waste cement can be regarded as a cheap and abundant calcium resource of which the weight fraction of calcium is about 30%. The alkaline earth metal components such as calcium or magnesium can be used as fixation media of anthropogenic CO_2 in the form of carbonates [13–15]. Thus, waste cement could be used as a fixation medium for the anthropogenic CO_2.

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 [16]. 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 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 be either disposed of in appropriate sites or recycled to the cement production industries.

The process feasibility of the CO_2 fixation process by waste cement could be enhanced when products that are more valuable can be obtained. 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 is also used in flue gas desulfurization processes to produce high-purity gypsum, which is required for the production of gypsum boards. Because of higher market prices of such high-purity calcium carbonate, the CO_2 fixation process by waste cement with the production of high-purity calcium carbonate could be more economically feasible than the simple fixation process or utilization for the cement production industry. In any applications, the CO_2 emission could be realized by treating waste cement with anthropogenic CO_2 at the corresponding amount of CO_2 that should have been released from virgin limestone. This study mainly focused on the production process of high-purity calcium carbonate in the precipitation process of calcium carbonate from the calcium-leached solution from waste cement. The precipitation rates of calcium carbonate and the purity of the products were experimentally studied in a laboratory-scale experimental apparatus. It was found that an addition of a small amount of seed crystals could significantly enhance the precipitation rates and the purity of the calcium carbonate product as well. The process is then examined in terms of the energy consumption and the operation cost based on the experimental results.

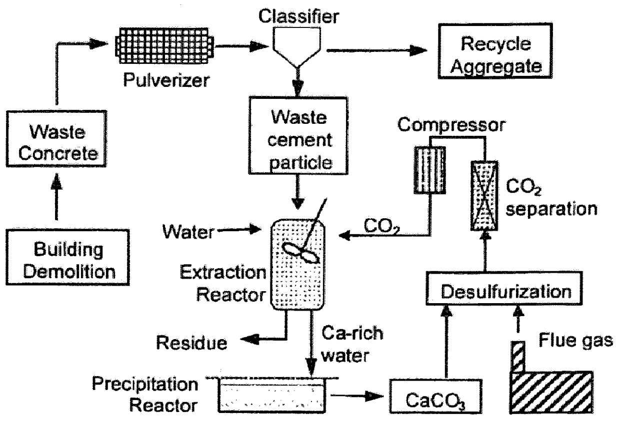

Figure 1. Outline of the recycling process for waste cement. Produced $CaCO_3$ will be sold as a high-purity reagent or as a desulfurization agent.

HIGH-PURITY $CaCO_3$ PRODUCTION BY WASTE CEMENT CARBONATION

A schematic flow diagram of the process is shown in Figure 1. Waste concrete generated from dismantled concrete buildings is mechanically pulverized and classified into aggregates and fine powders of waste cement. The waste cement powders are placed in the extraction reactor with water, after which pressurized CO_2 is supplied to the reactor. In the reactor, calcium ions are leached out into the aqueous phase. The CO_2 used for the extraction reaction is captured from the flue gas of a thermal power plant. The extraction reaction proceeds according to the following equations:

- Dissolution of CO_2 in water

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (2)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad (3)$$

- Leaching of calcium ions from the waste cement

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 6H^+ \rightarrow 3Ca^{2+} + 2SiO_2 + 6H_2O \quad (4)$$

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \quad (5)$$

After a given extraction period, the aqueous solution phase is transferred to the precipitation reactor after filtration. In the precipitation reactor, calcium carbonate is precipitated by reducing the CO_2 pressure.

- Precipitation of calcium carbonate

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow \quad (6)$$

The obtained calcium carbonate can be used as a flue gas desulfurization reagent. The efficiency of this process depends on a variety of operating conditions, such as the ratio of waste cement/water in the slurry, CO_2 pressure, temperature, and the stirring speed. In the following experimental section, the influences of these conditions on the reaction kinetics are examined, based on laboratory-scale experimental studies. The purity of the calcium carbonate produced is significant in the cost estimation of this process. A $CaCO_3$ purity of >95% is required for gypsum board production for commercial use. Ultrahigh-purity $CaCO_3$ (>99.5%) is required for fine chemical or ceramics production applications.

EXPERIMENTAL

Characterization of the Waste Cement Sample

The waste cement sample used in this study was kindly supplied by Tateishi Construction Corp. (Tokyo, Japan). The sample consists of fine particles obtained as a by-product 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 elemental analysis. About 11% {=100 × [(27.3 − 24.3)/27.3]} of the calcium was found to be carbonated already, based on thermogravimetric measurements with a differential thermal analyzer (TGD-9600, Ulvac, Tokyo, Japan).

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 ultrahigh-purity water. A gaseous CO_2 flow was continuously supplied to the reactor. The reactor was immersed in a constant temperature bath, and the reaction temperature was 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 0–1000 rpm.

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

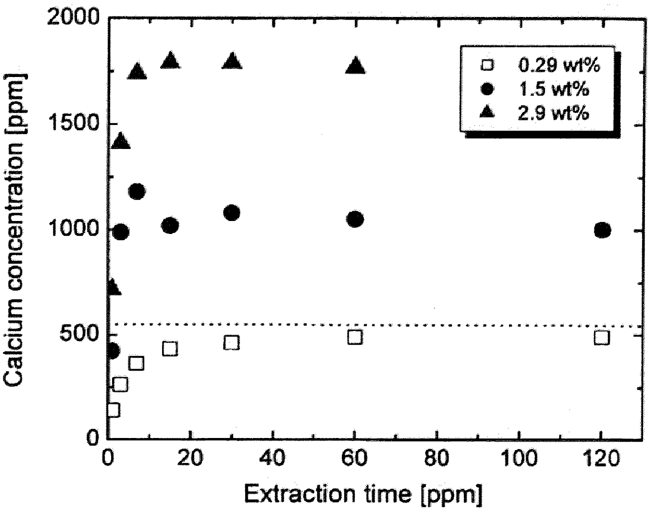

Figure 2. Change in concentration of calcium ions for various initial amounts of waste cement particles. Temperature = 323 K, stirring rate = 900 rpm, and p_{CO_2} = 3.0 MPa. The dotted line on the graph shows the saturated concentration of calcium under the extraction conditions used.

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, and the CO_2 pressure (p_{CO_2}). 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_{CO_2} (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 maximum thermodynamic solubility ($[Ca^{2+}]_{sat}$ = 592 ppm) of the calcium ions corresponding to the present experimental conditions. The solubility was calculated based on the solubility product of calcium carbonate at 323 K (pK_{sol} = 8.55, calculated). For conditions with larger C/W ratios (that is, 1.5 and 2.9 wt % of the waste cement), the observed concentration of calcium ions in the solution phase exceeded the predicted solubility within 5 min of the reaction time. On the other hand, for the case with the lowest C/W ratio (0.29 wt %), the observed concentration of calcium ions never exceeded the thermodynamic solubility.

The apparent extraction rate described above could be explained by the difference between the extraction rate of calcium ions from the waste cement and the precipitation rate of the extracted calcium ions with

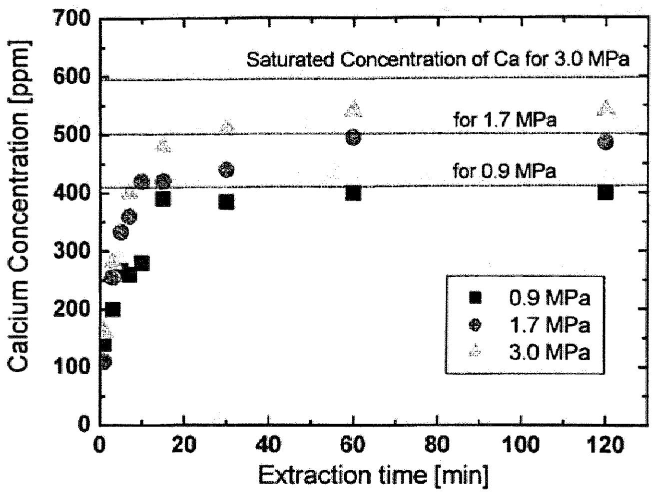

Figure 3. Change in concentration of calcium ions at various partial pressures of gaseous CO_2. Temperature = 323 K, stirring rate = 900 rpm, and amount of waste cement = 1.0 g. The dotted lines on the graph show the saturated concentrations of calcium under the extraction conditions used.

carbonate ions as calcium carbonate. For the cases with larger C/W ratios, where an abundant amount of waste cement is available for the extraction reaction, the extraction rate would be much higher than the precipitation rate, especially during the initial stage of the reaction. This explains the supersaturation observed during the initial stage of the extraction reaction for the cases with larger C/W ratios. As the extraction reaction proceeds, the concentration of calcium ions in the aqueous phase would increase and the amount of waste cement available for the extraction reaction would decrease. Both these conditions would decrease the extraction rate, whereas the precipitation reaction rate would be increased, which explains the decrease in the apparent extraction reaction rate observed during the later stage of the extraction reaction. The higher C/W ratio increases the rate of calcium ion extraction from the waste cement. However, the portion of calcium extracted from the waste cement in a given extraction time is smaller for the conditions with higher C/W ratios. As a result, a larger amount of unreacted waste cement should be recycled, or a larger amount of waste stream (that is, residues) will be generated in the process. On the contrary, a larger amount of water is necessary for the cases with lower C/W ratios. Thus, the required C/W ratio should be determined by taking these trade-offs into consideration.

Figure 3 shows the influence of the CO_2 pressure (p_{CO_2}) on the concentration of calcium ions over time, with a fixed stirring rate (900 rpm), temperature (323 K), and initial C/W ratio (1.0/350) (weight fraction of waste cement is 0.29 wt %). 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 rate was found to increase when the average size of the waste cement particles was decreased. 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 (291–353 K). 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 thus 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, under given extraction conditions, was transferred to the precipitation reactor after filtration through a sintered metal filter (5 μm mesh). The precipitation reactor is a vessel with a 300-mL inner volume made of reinforced glass. The precipitation 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 (P-4010, Hitachi).

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 thermo gravimetric method with a differential thermal analyzer (DTG-60H, Shimadzu, Kyoto, Japan). The thermogravimetric analysis indicated that the content of precipitated $CaCO_3$ was >98% (dry base). These results indicate that high-purity $CaCO_3$, which is suitable for use in the desulfurization 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 influence of the stirring rate on the concentration of calcium in the solution phase is shown in Figure 4. The calcium concentration decreased gradually over time. 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

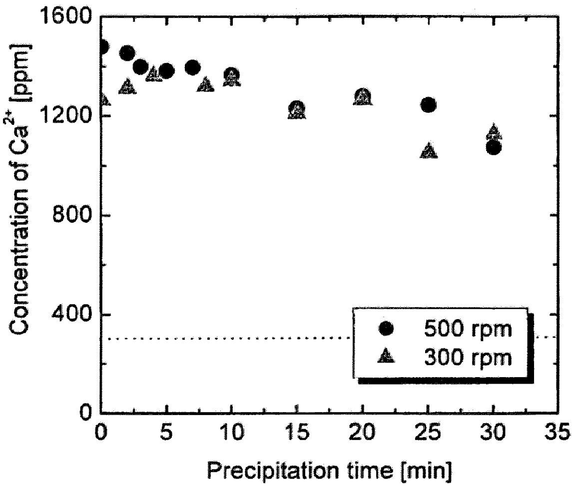

Figure 4. Influence of stirring rate on time course of calcium ion concentration in the solution. Initial solution volume = 200 mL, partial pressure of CO_2 = 0.2 MPa, precipitation temperature = 303 K, amount of $CaCO_3$ seed crystal = 0.05 g. The dotted line on the graph shows the saturation concentration of Ca^{2+} under these conditions, calculated using thermodynamic considerations.

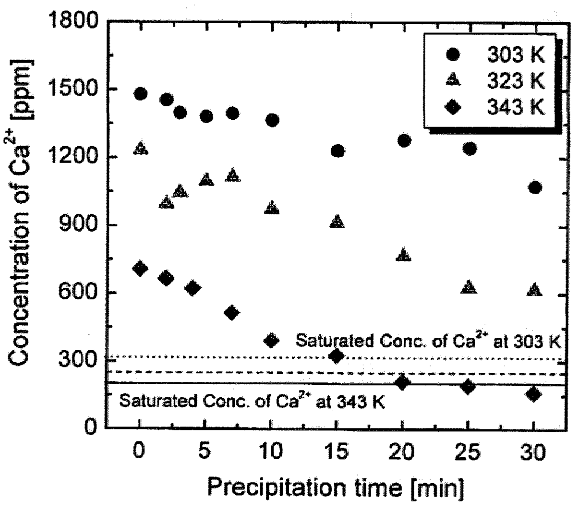

Figure 5. Influence of precipitation temperature on time course of calcium ion concentration in the solution. Initial solution volume = 200 mL, partial pressure of CO_2 = 0.2 MPa, stirring rate = 500 rpm, amount of $CaCO_3$ seed crystal = 0.05 g. The dotted, dashed, and solid lines on the graph show the saturation concentrations of Ca^{2+} under these conditions, calculated using thermodynamic considerations.

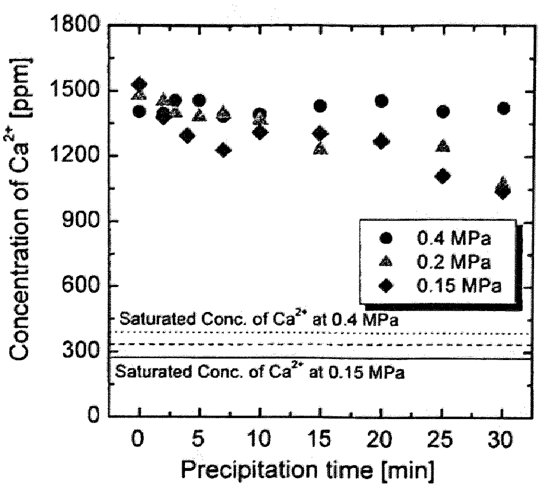

Figure 6. Influence of partial pressure of CO_2 on time course of calcium ion concentration in the solution. Initial solution volume = 200 mL, precipitation temperature = 303 K, stirring rate = 500 rpm, amount of $CaCO_3$ seed crystal = 0.05 g. The dotted, dashed, and solid lines on the graph show the saturation concentrations of Ca^{2+} under these conditions, calculated using thermodynamic considerations.

precipitation process for the stirring conditions studied. Figure 5 shows the influence of the temperature on the change in the concentration of dissolved calcium ions. The decreasing rate of the dissolved calcium ions can be regarded as the precipitation rate of $CaCO_3$. The precipitation rate increased with increasing temperature. It can be considered that a driving force for the precipitation reaction is the degree of supersaturation, which is defined as the ratio of the actual calcium concentration to the thermodynamic equilibrium concentration. Despite the greater degree of supersaturation for the lower-temperature conditions, the precipitation rate is lower, a result that suggests that the precipitation rate is controlled by some kinetic factor that will be increased with the temperature. Figure 6 shows the influence of the CO_2 pressure on the precipitation rate. The precipitation rate of $CaCO_3$ decreased with increasing CO_2 pressure, attributed to the increase in the solubility of calcium under high CO_2 pressure conditions, and this increases the driving force for the precipitation. Figure 7 shows the influence of the amount of $CaCO_3$ seed crystal on the precipitation rate. An increase in the amount of the seed crystal resulted in an increased precipitation rate, arising from 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; that is, that a lower solubility and higher surface area enhance the crystallization or precipitation rate of crystals.

PROCESS DESIGN AND SIMULATION FOR THE DESULFURIZATION 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 98%, can be produced by this process.

In this section, it is assumed that the present process is used in a process for desulfurization 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

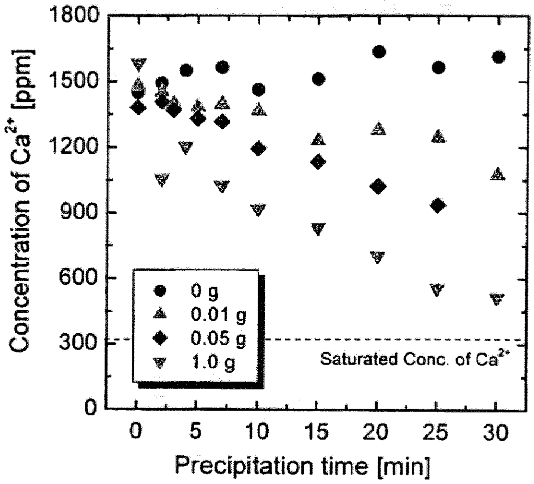

Figure 7. Influence of amount of seed crystal on time course of calcium ion concentration in the solution. Initial solution volume = 200 mL, precipitation temperature = 303 K, stirring rate = 500 rpm, partial pressure of CO_2 = 0.2 MPa. The dashed line on the graph shows the saturation concentration of Ca^{2+} under these conditions, calculated using thermodynamic considerations.

flow is shown in Figure 1. The amount of $CaCO_3$ required for the wet desulfurization process of a 500-MW coal-fired plant is 5.0 metric tons (t)/h. The amount of waste cement necessary for the desulfurization 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 ultrahigh-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 that shown in Figure 1, except that the high-purity calcium carbonate product (~98% purity) is further purified to 99.9% by redissolution and recrystallization processes. The production rate is assumed to be 1000 t 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 desulfurization and consequent separation and pressurization.

The following operations were considered in the estimation of the energy consumption and the cost of the process.

CO_2 Capture and Separation

The CO_2 will be captured from the flue gas of a thermal power plant by an amine absorption/desorption process, and the energy and cost for this CO_2 capture are cited from the literature [17]. It was also assumed that the waste heat of the thermal power plant would be available for stripping of the CO_2 from the amine solution.

CO_2 Pressurization

High-pressure CO_2 in the extraction reactor would increase the rate of calcium ion extraction from the waste cement. It was assumed that the captured CO_2 is pressurized from 0.1 MPa (atmospheric pressure) to 3.0 MPa. The energy required for the pressurization was estimated by assuming an isothermal compression process with 90% efficiency. The operation cost was estimated based on the unit price of the electric power (USD 0.1/kWh) required for the compression process. The capital cost of the compression facility was estimated using a 5% rule of thumb: that the capital cost is 5% of the operational cost. The energy consumption for the construction of the facility was also estimated using the 5% rule of thumb.

Pulverization and Classification of the Waste Cement

The waste cement is pulverized and classified before use, given that raw waste cement is normally supplied with an average particle size of about 5 mm, and the pulverization is essential for enhancing the extraction rate. Pulverization energy for the waste cement was estimated based on Bond's equation (Eq. 7) [18], assuming pulverization from a diameter of 5 mm to 200 μm. The power consumption W(m$^{1/2}$ kWh^{-1} t^{-1}) for pulverizing 1 kg of a powder with the diameter of d_{p1} to the diameter of d_{p2} is given by

$$W = k_B\left(\frac{1}{\sqrt{d_{p2}}} - \frac{1}{\sqrt{d_{p1}}}\right) \tag{7}$$

where k_B is a constant depending on the powder material. In this study, it is assumed that $k_B = 1.345 \times 10^{-1}$ m$^{1/2}$ kWh^{-1} t^{-1} for the waste cement powder, which is used for cement clinkers. The 5% rule of thumb was used to estimate the capital cost and the energy consumption.

Extraction Process

The extraction of the calcium ions is assumed to take place at 323 K and p_{CO_2} = 3.0 MPa, with a weight fraction of waste cement of 2.9%, which corresponds to the highest initial reaction rate in the experimental results in this study. The required reactor volume was calculated using the mass flow rate of the waste cement supply, with a retention time of 3.0 min. The stirring power—the main energy consumption sector in the extraction process—was estimated by the following scale-up scheme; the stirring power consumption per unit volume of the scaled-up reactor was equalized to that for the extraction reactor used in the experimental studies. The stirring power for the experimental reactor was estimated based on Nagata's equation [19], where the power consumption for the stirring operation is given by

$$W = N_p \rho n^3 d^5 \tag{8}$$

where N_p is the dimensionless power number, ρ (kg/m^3) is the density of the fluid, n (s^{-1}) is the stirring rate, and d(m) is the paddle diameter. The power number is given by

$$N_p = \frac{A}{\mathrm{Re}} + B\left(\frac{1000 + 1.2\,\mathrm{Re}^{0.66}}{1000 + 3.2\,\mathrm{Re}^{0.66}}\right)^{P}\left(\frac{Z}{D}\right)^{(0.35 + b/D)} \sin\theta^{1.2} \tag{9}$$

where Z (m) and D (m) are the height and the diameter of the stirring vessel, respectively; b is the height of the paddle from the bottom of the reactor; and θ is the angle of the paddle with respect to the stirring shaft. Re is the Reynolds number, defined by

$$\mathrm{Re} = \frac{\rho n d^2}{\mu} \tag{10}$$

The parameters A, B, and P, respectively, are given by

$$A = 14 + \frac{b}{D}\left[670\left(\frac{d}{D} - 0.6\right)^2 + 185\right] \tag{11}$$

$$\log B = 1.3 - 4\left(\frac{b}{D} - 0.5\right)^2 - 1.14\left(\frac{d}{D}\right) \tag{12}$$

$$P = 1.1 + 4\left(\frac{b}{D}\right) - 2.5\left(\frac{d}{D} - 0.5\right)^2 - 7\left(\frac{b}{D}\right)^4 \tag{13}$$

The capital cost for the extraction reactor was estimated based on the material cost for constructing the reactor. The reactor material is stainless steel, and the amount needed was calculated using the size and the minimum wall thickness assigned by the Japanese Industrial Standards (JIS) for high-pressure vessels. The operating cost for the extraction reactor was estimated based on the electric power price.

Precipitation Process

The precipitation process was carried out under a reduced CO_2 pressure of 0.1 MPa, and the precipitated calcium carbonate crystals was separated in a thickener. The reactor volume necessary for the precipitation process was calculated based on a retention time of 3 min, which was determined by extrapolating the experimental results for the amount of seed crystal used at 2.85 wt % of water. The power consumption for the stirring and capital cost for the precipitation reactor was estimated by the same methods as those used for the extraction process. The operating cost of the extraction reactor was estimated based on the electric power price.

Storage of the Waste Cement and $CaCO_3$

It was assumed that the raw waste cement and the $CaCO_3$ product would be stored in a storage silo. The cost of building this was estimated based on the cost for an actual facility (10 t/h) with a scaling-up rule of thumb that the construction cost is a 6/10 exponential function of its capacity.

Wastewater Treatment

The water necessary for the extraction reaction could be recycled after the precipitation operation. It would be necessary to treat the water because some unnecessary components that are soluble in water would be accumulated after a number of reuse cycles. The cost for the wastewater treatment was estimated from the amount of wastewater and a unit cost for wastewater treatment with 100 cycles of water reuse before treatment.

Industrial Waste Treatment and Transportation

After the extraction of calcium ions from the waste cement, the residue should be transported and disposed of as industrial waste. On the other hand, because the raw waste cement is also industrial waste, the acceptance of waste cement would produce an income depending on the amount used. However, the transportation costs of these waste streams should be considered. The cost for industrial waste disposal is about 38 USD/t, based on the current cost in Japan. The transportation cost was 9.5 USD/t.

Further Purification of Calcium Carbonate

Further purification is necessary to obtain ultrahigh-purity calcium carbonate, given that the 98% purity is much lower than that required for fine chemical or ceramics production. The purification was assumed to consist of two processes: (1) dissolution of the calcium carbonate with 1.0 MPa of CO_2 and (2) recrystallization of calcium carbonate from the solution by a decrease in the CO_2 pressure. The reactor volumes for both operations were calculated using the dissolution/precipitation reaction rates. The dissolution rate was determined by the mass-transfer coefficient derived for spherical particles and the solubility as a function of the Reynolds number for stirring. The precipitation rate was determined from the experimental results obtained in this study. Based on these experimental results, we assumed that the precipitation rate could be accelerated to be as fast as that of the calcium dissolution, by injection of seed crystals of $CaCO_3$.

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 desulfurization 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 is shown in the first column of Table 1. The three main energy-consuming operations are 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 compared 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 wastewater treatment (~9%), as well as the above-mentioned energy-intensive operations. About 90% of the total capital cost is for the construction of the wastewater treatment plant and a silo for the waste cement. As a result, the cost for the production of calcium carbonate in this example is

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

Unit operation	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
Wastewater 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 ultrahigh-purity $CaCO_3$ for use as a reagent needed in the proposed process in the 500-MW coal-fired thermal power plant.

Unit operation	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
Wastewater treatment	—	5.4	107	112
Industrial waste treatment and transportation	—	60	—	60
Total	0.024	92	230	323

USD 136 per metric ton. This number is comparable with the commercial price of USD 200–350 for heavy calcium carbonate produced from natural limestone.

The results for the production of ultrahigh-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 operations. The energy required for the extraction and precipitation reactions was almost negligible compared 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 wastewater treatment (~ 6%), in addition to the above-mentioned energy-intensive operations. About 90% of the total capital cost is the construction of the wastewater 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, which again is much lower than the present market price of ultrahigh-purity calcium carbonate, USD 10,000 per metric ton.

The cost estimated in this study may still be able to be substantially reduced. 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 in such applications as roadbed material, raw material for adsorbent, and clay substitution. 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 ultrahigh-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 desulfurization process of the flue gas of a thermal power plant.

CONCLUSIONS

The proposed process for producing calcium carbonate from waste cement by using pressurized CO_2 is highly promising for flue gas desulfurization in terms of the cost and energy consumption. In addition, simultaneous reduction of the two waste streams—CO_2 and waste cement—could be achieved by the proposed process. The total energy consumption for the $CaCO_3$ production needed in the desulfurization 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 light $CaCO_3$). We also examined the production of ultrahigh-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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