Carbon Reduction of Gypsum Produced from Flue Gas Desulfurization

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In this study, the changes in the chemical form of calcium on reduction with solid carbon were investigated in order to develop a process for the regeneration of CaO from spent gypsum at low temperatures. Calcium sulfate dihydrate was used as a model compound for gypsum; it was mixed with solid carbon and heated to a terminal temperature of 1100 °C. CaO was produced from 900 °C, after the formation of CaS, by the reaction of $CaSO_4$ and CaS, with the consumption of solid carbon. There is an optimum amount of solid carbon that should be added to produce CaO efficiently from gypsum. Kinetic analyses of the formation of CaO from gypsum by carbon reduction during heat treatment of a mixture of solid carbon and gypsum were conducted.

1. Introduction

Limestone is a self-sufficient resource in Japan, and the reserve as of 2009 was 27.2 Gt. The annual amount of limestone produced in Japan is 130 Mt. Japan has an approximately 200 y supply of limestone. A large amount of limestone is consumed as a raw material in the cement, lime, and steel industries; recently, there has been a move towards recycling spent concrete and spent gypsum. For example, methods for the regeneration of raw materials such as aggregates, cement, and desulfurization agents from waste concrete have been studied (Sakai et al, 2007). Reuse of spent gypsum board as a raw material has been examined. However, the loss of strength and the increased production costs of the gypsum board are problems when spent gypsum is used as the raw material, because of the fine crystal size of bassanite ($CaSO_4 \cdot 0.5H_2O$) derived from spent gypsum. Recrystallization methods for spent gypsum have been studied, but have not yet been commercialized (Kojima et al., 2004). Since the separation of paper and other impurities in the spent board are necessary, the recycling ratio of spent gypsum board is at present less than 10 %, so more than 90 % of spent gypsum is disposed of in landfill sites. Recently, hydrogen sulfide evolution in reclamation sites has become a serious problem, as a result of bacterial reduction of spent gypsum (Kikuchi et al., 2001).

Calcium oxide is widely used for desulfurization in power plants, the removal of impurities such as sulfur and phosphorus in the steel industry, and the recovery of sodium hydroxide from various liquid wastes. The spent gypsum can be converted to calcium oxide by heating at temperatures above 1000 °C in air. Regeneration methods using a reducing agent to obtain calcium oxide at low temperatures have also been studied (Turkdogan and Vinters, 1976; Kuusik et al., 1985; Kutsovskaya et al., 1996; Strydom et al., 1997; Tao et al., 2001; Okumura et al., 2003). The advantages of reduction using solid carbon are that inexpensive reducing agents such as coal and heavy-oil ash can be used, and the reducing agents are easy to handle. Although many studies of carbon reduction of gypsum at temperatures above 1000 °C have been reported (Turkdogan and Vinters, 1976; Kutsovskaya, 1996;

Strydom et al., 1997; Tao et al., 2001), there have been few studies of the conversion characteristics of gypsum to calcium oxide at low temperatures. Many studies of the reduction behavior of calcium sulfate have been performed by examining the weight changes of samples and the evolution of SO_2 gas (Turkdogan and Vinters, 1976; Strydom et al., 1997). However, it is difficult to estimate the change in the chemical form of calcium precisely from the amount of SO_2 generated because calcium sulfide, which is generated from calcium sulfate by carbon reduction, reacts with SO_2 to form elemental sulfur (Sohn and Kim, 2002a; Sohn and Kim, 2002b; Choi et al., 2007a; Choi et al., 2007b).

In this study, in order to develop a process for the regeneration of calcium oxide from spent gypsum at low temperatures, the reduction behavior of gypsum to calcium oxide by solid carbon was investigated. The mixture of gypsum and solid carbon was heated to final temperatures ranging from 700 to 1100 °C in a nitrogen stream, and changes in the calcium chemical form were examined in detail. Heavy-oil ash was used as the solid carbon reducing agent, thereby using resources generated by oil-fired power plants. The effects of the amount of carbon added on the change in the chemical form of calcium during the heat treatment of calcium sulfate were examined. Kinetic analyses of the reduction of calcium sulfate were performed and the optimum amount of solid carbon for the efficient production of calcium oxide from calcium sulfate was determined.

2. Experimental

2.1 Sample

Calcium sulfate dihydrate (Nakarai Tesque, Kyoto, Japan) was used as a model for spent gypsum. A heavy-oil ash, which contained carbon as the main component, was used as the reducing agent (referred to as "solid carbon"). It contained 67.7 % carbon and 1.4 % hydrogen (on a dry ash-free basis), and 21.0 % volatile matter and 14.4 % ash (on a dry basis). Figure 1 shows particle size distribution curves for the solid carbon and the calcium sulfate dihydrate. The average particle sizes of these samples were 31 and 61 μm, respectively. Calcium sulfate dihydrate and solid carbon were mixed physically in molar ratios of C/Ca = 0 to 2, and the mixtures were used in CaO regeneration experiments.

2.2 Heat treatment

The heat treatment of the mixture was carried out in a horizontal fixed-bed reactor equipped with stainless-steel tubing of diameter 30 mm as the reactor tube. A sample in an alumina boat was placed at the center of the reactor, and nitrogen was supplied to the reactor at a flow rate of 800 mL-NTP/min. The reactor was heated to a maximum temperature of 1100 °C at a heating rate of 10 °C/min, and was kept for a maximum of 1 h at the desired temperature. The reactor was cooled to room temperature, and thus the heat-treated sample was obtained.

2.3 Analysis

Various chemical forms of calcium were analyzed quantitatively as follows. CaS reacts with oxygen to form a sulfate, although CaO and $CaSO_4$ are stable in air at high temperatures (Strydom et al., 1997). Thus, the amount of CaS in the sample was determined from the weight increase as a result of oxidation of the sulfide to the sulfate. Thermogravimetric-differential thermal analysis (Thermoplus 8120, Rigaku, Tokyo, Japan) was used to determine the amount of CaS in the heat-treated sample. The sample was heated at 10 °C/min to 1000 °C under air. The amount of $CaSO_4$ was calculated from the amount of sulfur other than sulfur present as CaS. The total sulfur in the sample was analyzed using a carbon/sulfur analyzer (EMIA-520, Horiba, Kyoto, Japan). The amount of CaO formed was calculated by subtracting the molar amounts of calcium present as CaS and $CaSO_4$ from the initial amount of calcium in sulfate form. The amount of carbon was determined using an HCN analyzer (MT-700, Yanaco, Tokyo,
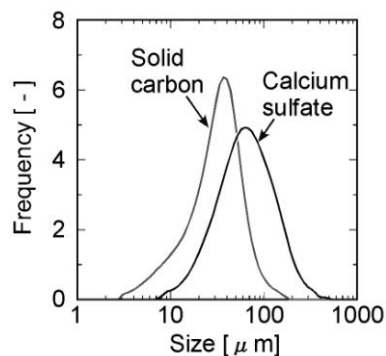

Figure 1: Particle size distributions of calcium sulfate dihydrate and solid carbon

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Japan). The particle size distribution and average particle size (d_{50}) were determined using a laser diffraction method (Microtrac HRA-X-100, Nikkiso, Tokyo, Japan).

3. Results and discussion

3.1 Effects of treatment temperature and carbon amount

Figure 2 shows the amounts of calcium oxide formed during heat treatment of samples with different mixing ratios of calcium sulfate and solid carbon at final temperatures ranging from 700 to 1000 °C in a nitrogen stream. The mixing ratio varied from C/Ca = 0 to 2.00. These samples were prepared by heating the mixture to the terminal temperature and cooling immediately. Formation of CaO was not observed for the mixing ratios C/Ca = 0 ($CaSO_4$ only) and 2.0 across the whole temperature range. Formation of CaO was identified at C/Ca = 0.25 above 800 °C and the amount of CaO increased with

Figure 2: Effects of C/Ca ratio on conversion of CaSO4 to CaO

increasing temperature. For the sample with C/Ca = 0.50, the formation of CaO began above 800 °C, CaO was rapidly produced at around 950 °C, and 90 % conversion was achieved at 1000 °C. For a sample containing more carbon (C/Ca = 0.75), the formation extent of CaO was 75 %, and was lower than that of the sample with C/Ca = 0.50. It was confirmed that for carbon reduction of $CaSO_4$, the formation of CaO started at around 800 °C, and the amount of CaO did not simply increase with increasing amounts of carbon.
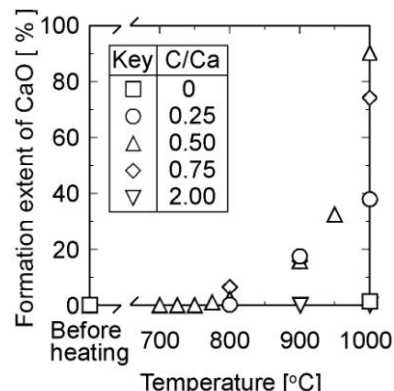
Figure 3 shows the changes in the chemical form of Ca and the unreacted carbon content with temperature during heat treatment of the sample with C/Ca = 0.25. Formation of CaS was observed at temperatures between 800 and 900 °C, and $CaSO_4$, CaS, and CaO coexisted at 900 °C. CaS disappeared and $CaSO_4$ and CaO were present in the heat-treated sample at 1000 °C. All the carbon disappeared by 900 °C, thus it is deduced that the carbon contributed to the reduction of $CaSO_4$ to CaS.
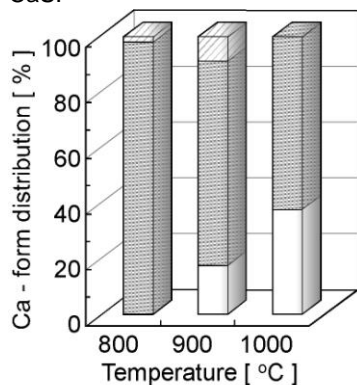

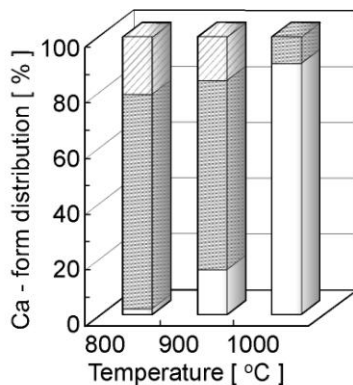Figure 3: Formation of CaO and CaS from $CaSO_4$ at C/Ca = 0.25
⬜ CaO, ▨ $CaSO_4$, ▧ CaS

Figure 4: Formation of CaO and CaS from $CaSO_4$ at C/Ca = 0.50
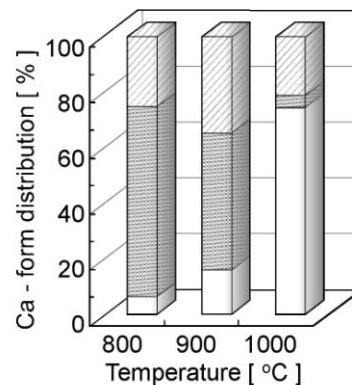⬜ CaO, ▨ $CaSO_4$, ▧ CaS

Figure 5: Formation of CaO and CaS from $CaSO_4$ at C/Ca = 0.75
⬜ CaO, ▨ $CaSO_4$, ▧ CaS

Changes in the chemical form of Ca and carbon content with temperature during heat treatment of the sample with C/Ca = 0.50 are shown in Figure 4. Three Ca chemical forms coexisted in the sample at 900 °C, as in the case of the sample with C/Ca = 0.25 shown in Figure 3. The amount of CaO increased rapidly and 90 % of the Ca had been converted to CaO when the temperature reached 1000 °C. The added carbon does not participate in the formation of CaO at 1000 °C, because all of it disappears by 900 °C.

Figure 5 shows the changes in the Ca chemical form and carbon content for the sample with C/Ca = 0.75; 24 and 35 % of the Ca existed in the samples at 800 and 900 °C, and there was more extensive formation of CaS than in the cases with C/Ca = 0.25 and 0.50; 20 % CaS was observed when the

temperature reached 1000 °C. In contrast, the amount of CaO was around 75 % at the same temperature, that is, the formation of CaO by the reaction of $CaSO_4$ and CaS was suppressed, although the reduction of $CaSO_4$ to CaS accelerated when the carbon content increased. It was realized that there is an optimum carbon addition amount for the formation of CaO from $CaSO_4$ by carbon reduction.

These results indicate that CaO can be formed from $CaSO_4$ by carbon reduction according to the following reactions.

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \text{ (g)} \tag{1}$$

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \text{ (g)} \tag{2}$$
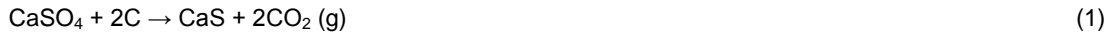
The carbon added is consumed in the reduction of $CaSO_4$ to CaS. Then the desired product (CaO) is produced by reaction of the intermediate (CaS) and the unreacted $CaSO_4$, that is, the carbon does not contribute to the formation of CaO, but the amount of CaO changes with the carbon content; as a consequence, the ratios of CaS and $CaSO_4$ change with carbon content.

3.2 Effects of reaction time

Figure 6 shows the formation of CaO and CaS from $CaSO_4$ in heating of a sample with C/Ca = 0.50 in a nitrogen stream at 900 °C for a specified time. The amount of CaO gradually increases with reaction time, and it was confirmed that 42 and 68 % of total calcium were converted into CaO for reaction times of 0.5 and 1.0 h, respectively. Turkdogan and Vinters (1976) examined the reduction of reagent-grade calcium sulfate and a powdered natural gypsum using graphite, coconut charcoal, coal char, and coal as reducing agents. They reported that the formation extent of CaO was 30 % at 900 °C for 160 min. The formation extent of CaO in this study reached 68 % after heating at 900 °C for 60 min. The reason for this high conversion is that the solid carbon and calcium sulfate particles used in these experiments were very fine.

3.3 Kinetic analysis of reduction of calcium sulfate

Based on the formation of CaS and CaO from $CaSO_4$, as expressed in Eqs.(1) and (2), and assuming that each rate can be expressed as a first-order reaction with respect to the $CaSO_4$, CaS, and C concentrations in the solid phase, the mass balances of the components are shown in Eqs. (3)–(6).

$$d[CaSO_4]/dt = -k_1[CaSO_4][C] - 3k_2[CaSO_4][CaS] \tag{3}$$

$$d[CaS])/dt = k_1[CaSO_4][C] - k_2[CaSO_4][CaS] \tag{4}$$

$$d[CaO])/dt = 4k_2[CaSO_4][CaS] \tag{5}$$

$$d[C])/dt = -2k_2[CaSO_4][C] \tag{6}$$

The rate constants can be expressed using the Arrhenius equation (Eq. 7).

$$k_i = k_{(i0)}\exp[-E/(RT)], \ (i = 1, 2) \tag{7}$$
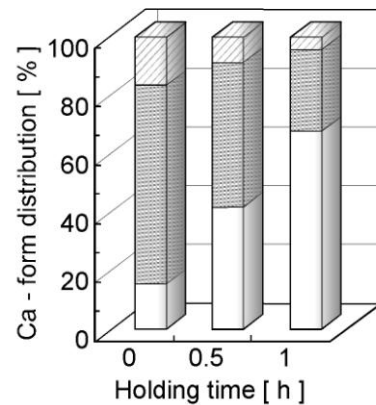
The initial conditions are as follows.

Figure 6: Formation of CaO and CaS from $CaSO_4$ in heating of sample with C/Ca = 0.50 at 900 °C
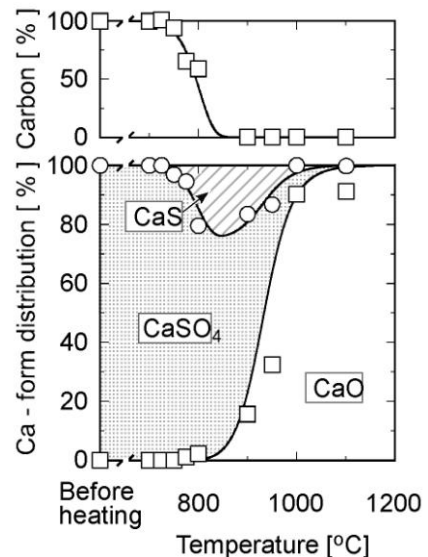
CaO, $CaSO_4$, CaS

Figure 7: Experimental and simulated results for changes in distribution of chemical form of Ca with temperature (C/Ca = 0.5). Solid lines show the simulated values
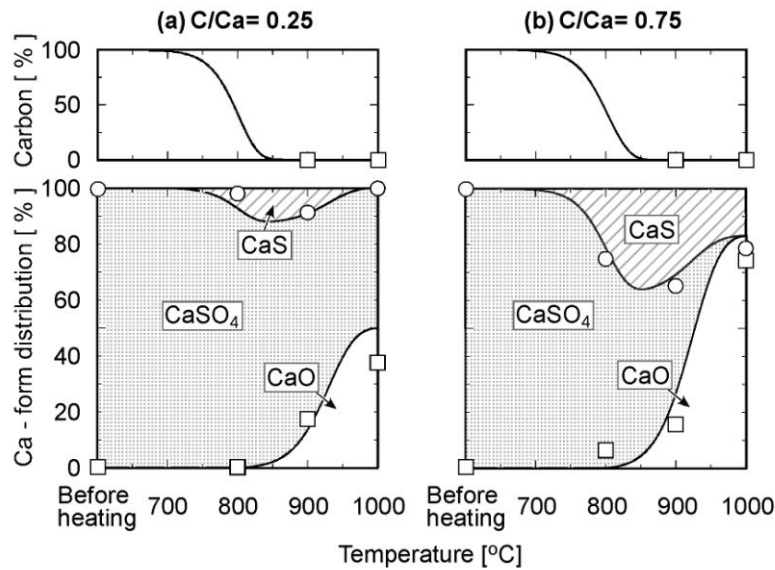
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Figure 8: Experimental and simulated results for changes in distribution of chemical form of Ca with temperature for (a) C/Ca = 0.50 and (b) C/Ca = 0.75

$[CaSO_4] = [CaSO_4]_0$, $[C] = [C]_0$, $[CaS] = [CaO] = 0$ at $t = 0$

The heating rate is represented in Eq. (8).

$$dT/dt = (10\ °C/min) \tag{8}$$

Figure 9: Experimental and simulated results for changes in distribution of chemical form of Ca with molar ratio of C to Ca

Simulated results for changes in the distribution of the chemical form of Ca with temperature for the sample with C/Ca = 0.50 are shown in Figure 7. The solid lines show the simulated values. The symbols in the figure show the experimental data. Open circles and squares show the total amount of Ca_{CaSO4} and Ca_{CaS}, and the amount of Ca_{CaO}, respectively. The kinetic parameters used here are $k_{10} = 3.2 \times 10^{15}$ mol^{-1} s^{-1}, $E_1 = 370$ kJ/mol, $k_{20} = 1.6 \times 10^{15}$ mol^{-1} s^{-1}, and $E_2 = 400$ kJ/mol. The fact that solid carbon is used for reduction of $CaSO_4$ and that it disappears at around 850 °C is shown by the simulated values. The formation of CaS by the reaction of $CaSO_4$ and carbon and the generation of the maximum amount of CaS at around 850 °C is also successfully simulated. It is also shown that the amount of CaO increased rapidly with decreasing CaS amounts with increasing temperature.

The simulated results for changes in the distribution of the chemical form of Ca with temperature for samples with C/Ca = 0.25 and C/Ca=0.75 are shown in Figure 8. The kinetic parameters are the same as those for the sample with C/Ca = 0.50. For the samples containing an excess or insufficient ratio of carbon to calcium, the experimental values are approximately in agreement with the simulated results.

The effects of carbon addition amounts on the distribution of the chemical form of Ca for the samples with C/Ca = 0 to 2.0 heated to 1000 °C are shown in Figure 9. The solid lines in this figure show the simulated values. It can be seen that the formation of CaO increases significantly with increasing C/Ca ratio and that the amount of CaS increases with further increases in the ratio after reaching a maximum with C/Ca = 0.50. Based on the stoichiometries of the reactions in Eqs. (1) and (2) and the experimental results in this study, the optimum ratio of added carbon to calcium for increasing CaO formation is considered to be C/Ca = 0.50.
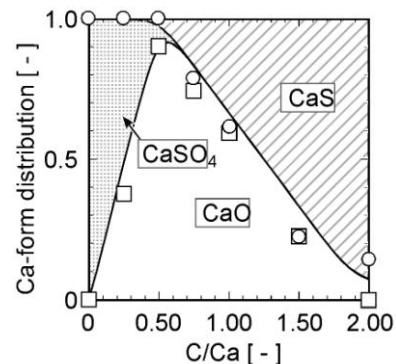
4. Conclusions

To develop a process for regeneration of CaO from spent gypsum at low temperatures, the formation of CaO by carbon reduction with solid carbon was investigated. The reduction of calcium sulfate to calcium sulfide was completed by 900 °C. CaO was then produced by the reaction of calcium sulfate and calcium sulfide at temperatures between 900 and 1000 °C. The ratio of solid carbon to calcium sulfate significantly influenced the production of calcium oxide. When the amount of carbon was insufficient to reduce the calcium sulfate, the production of calcium oxide was low as a result of a shortage of sulfide. However, calcium sulfide tended to be formed predominantly in the case of an excess of carbon to calcium sulfate. It is necessary to control the mixing ratio of carbon and calcium sulfate to C/Ca = 0.50 to obtain calcium oxide efficiently. Kinetic analyses of the reactions for the formation of calcium sulfide from calcium sulfate by reduction with carbon (Eq. 1) and for the formation of calcium oxide from calcium sulfate and sulfide (Eq. 2) were conducted. Kinetic parameters that could express the changes in the chemical form of calcium in the heat treatment of samples with different carbon contents were determined.

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