Development of a New Dry Flue Gas Desulfurization Process Utilizing Calcium Silicate Hydrate in Waste Concrete

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Abstract

The reaction kinetics of SO_2 removal was studied by laboratory-scale experiments to examine the potential desulfurization efficiency by the waste cement particles. Desulfurization experiments for $Ca(OH)_2$ and calcium carbonate ($CaCO_3$) were also conducted under the same conditions for comparison. Laboratory experimental studies showed that the waste cement particles have a sufficiently high reaction rate with gaseous SO_2, under the temperature conditions of 30 ~ 400 ^oC. The waste cement would be applicable for the desulfurization process, especially under the lower temperature conditions such as 30 ^oC, under which the desulfurization rate is comparable with that of calcium hydroxide, which has been commonly used as a desulfurization agent but much more expensive than the waste cement. The use of waste cement would be a promising option for a dry desulfurization process.

Introduction

Flue gas desulfurization (FGD) has been developed to reduce the sulfur dioxide (SO_2) emission associated with coal or oil combustion since early 1970s. Various types of the flue gas desulfurization (FGD) processes have been developed, including wet, semi-dry, and dry FGD processes [1]. Wet FGD process has been widely used for large-scale SO_2 emission sources because of its high SO_2 recovery efficiency. However, a large amount of water is necessary to operate the wet FGD processes, and therefore, it may not be appropriate to apply them to emission sources located where water supply is insufficient and costly, *e.g.* inland China. Dry FGD processes would be more suitable for such a location, and development of low-cost FGD processes with high SO_2 recovery efficiencies should be necessary to meet the sharp increase of the demand on the FGD processes.

Recently, a new type dry FGD process by utilizing calcium silicate hydrate gel (C-S-H gel) as a desulfurization agent has been developed [2]-[6]. The C-S-H gel is generated from silica and calcium hydroxide ($Ca(OH)_2$) by the reaction at the surface of fly-ash particles Sufficiently high SO_2 recovery efficiencies could be realized by the process under the temperature at 57-400 ^{o}C, which is far below the normal operation temperature of 900 ^{o}C for the processes using conventional agents such as $Ca(OH)_2$, or $CaCO_3$.

In this paper, we proposed a new dry desulfurization process by utilizing waste cement particles. Since hydrated cement is composed of alkali calcium compounds such as $Ca(OH)_2$, C-S-H gel, it is expected that waste cement particles have a high reactivity with SO_2. The following reaction scheme can be considered between waste cement and SO_2,

Direct substitution of SO_2:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + 2H_2O \quad (1)$$

$$3CaO\cdot 2SiO_2\cdot 3H_2O + 3SO_2 \rightarrow 3CaSO_3 + 2SiO_2 + 3H_2O \quad (2)$$

Oxidation of Calcium sulfite ($CaSO_3$) (aerobic condition):

$$CaSO_3 + 1/2\ O_2 \rightarrow CaSO_4 \quad (3)$$

The reaction kinetics of SO_2 removal was studied by laboratory-scale experiments to examine the potential desulfurization efficiency by the waste cement particles. Desulfurization experiments for $Ca(OH)_2$ and calcium carbonate ($CaCO_3$) were also conducted under the same conditions for comparison.

Experimental

Properties of the waste cement particle

The waste cement sample used in this study was supplied by Tateishi Construction Corp. The sample is fine particles obtained as a byproduct in a commercialized plant of waste concrete for recycling aggregates. The size distribution of the particles was measured by a laser-scattering particle size measurement apparatus (Shimadzu, SALD1100). The diameter of the waste cement particles was distributed over the range of 10 ~ 200 μm, with a peak located at about 25 ~ 40 μ m (surface area based), and about 80 μ m (volume based). The elemental composition of the sample was analyzed by X-ray fluorescence technique (JEOL, JSX-3220), and the weight fraction of calcium was 27.3 %. The maximum potential capacity for desulfurization by the sample is 0.44 t of SO_2 ($= 1 \times 0.273 \times 64 / 40$) per ton of the waste cement assuming complete reaction of the calcium content in the waste cement with SO_2.

SO_2 removal rate measurement

The reaction rate of gaseous SO_2 and the waste cement particle was measured by thermal gravimetry - differential thermal analysis (TG-DTA, Shimadzu, H60). Figure 1 shows the schematic drawing of the experimental apparatus. The feed gas is supplied from a cylinder of pre-mixed gaseous mixture of 1000 ppm SO_2 balanced with air. The feed gas will be reacted with the waste cement particles placed on the sample alumina cell, and the

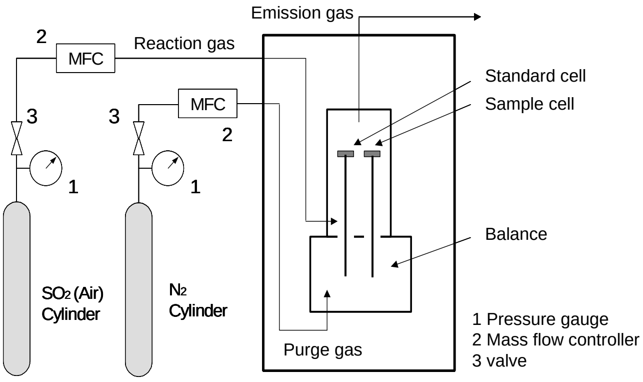

Figure 1. Schematic drawing of experimental apparatus for SO_2 removal rate measurements.

Table 1. Experimental conditions for SO_2 removal rate measurements

Gas flow rate	100 mL / min
Gas composition	SO_2 1000 ppm, Dried Air balance
Temp. rising rate	25 ^{o}C / min
Reaction Temp.	30, 60, 100, 200, 300, 400 ^{o}C

weight change was measured. The reaction temperature was changed in the range of from 30 to 400 ^{o}C. The flow rate of the feed was controlled by a mass flow controller. Experimental conditions are summarized in Table 1.

Results and Discussions

The weight of the waste cement was increased with an increase of the reaction time at the initial stage as shown in Figure 2. The weight increase is due to the generation of $CaSO_3$ from the calcium contents in the waste cement. The initial reaction rate up to 10 min was decreased with an increase in the reaction temperature, while the maximum amount of the SO_2 removal per unit mass of the waste cement was increased with the reaction temperature. Especially, high desulfurization reaction rate was observed under 60 ^{o}C. In Figure 3, the reaction rates of the SO_2 removal were compared among the three agents (waste cement, $Ca(OH)_2$ and $CaCO_3$) under 100 ºC. Although the maximum

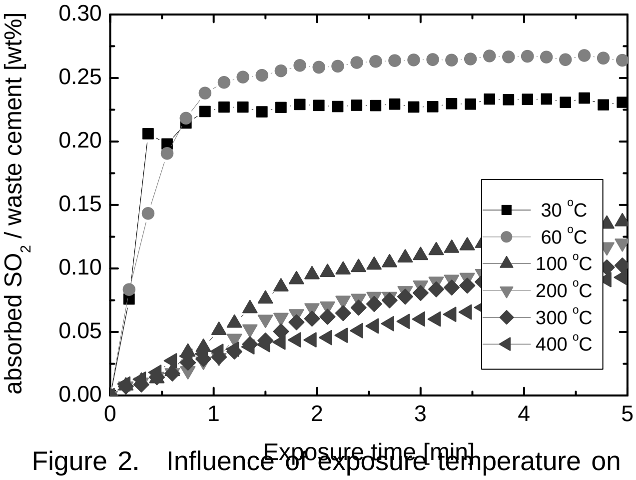

Figure 2. Influence of exposure temperature on time course of the absorbed SO_2 / waste cement particle weight percent.

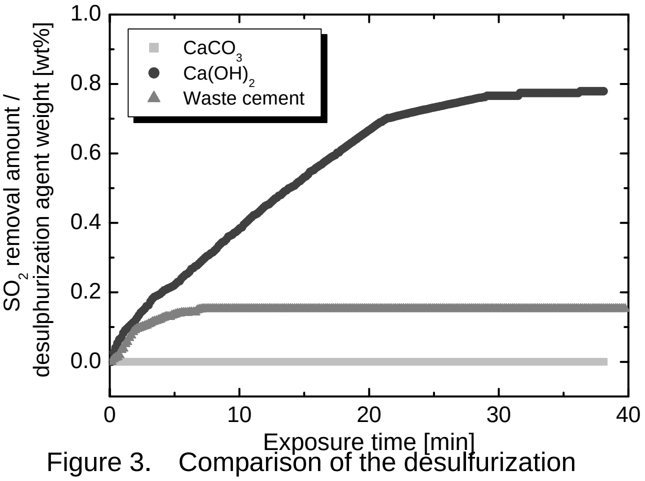

Figure 3. Comparison of the desulfurization reaction rate among three agents at 100 ºC.

capacity per weight of the waste cement is about 1/4 times as large as that of $Ca(OH)_2$, and the reaction rate at the initial stage is almost equivalent to that of $Ca(OH)_2$, while no reactivity was observed for $CaCO_3$ with SO_2.

Conclusions

Laboratory experimental studies showed that the waste cement particles have a sufficiently high reaction rate with gaseous SO_2, under the temperature conditions of 30 ~ 400 ºC. Especially, high desulfurization reaction rate was observed under 60 ºC. The waste cement would be applicable for the desulfurization process, especially under the lower temperature conditions such as 30 ºC, under which the desulfurization rate is comparable with that of calcium hydroxide, which has been commonly used as a desulfurization agent but much more expensive than the waste cement. The use of waste cement would be a promising option for a dry desulfurization process.

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