REMOVAL OF SO$_2$ FROM FLUE GAS USING ULTRAFINE CaO PARTICLES

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Introduction

Development of an economical method for removing SO$_2$ from the flue gas produced by combustion facilities is urgently needed to mitigate the world-threatening acid rain problem.

Although numerous wet and dry desulfurization processes have been developed and applied[7, 12], the most cost-efficient dry process such as the limestone injection method, has a poor SO$_x$-removal efficiency ($\leqq$ 30 %) because of the low reaction rate of CaO with SO$_2$[8]. This particular drawback led to the present study in which we improve this reaction rate via reduction of CaO particles to an ultrafine (UF) size, i.e., diameter (d_p) < 0.1 μm, being accomplished by employing the laser ablation method. We discovered that the reaction rate of UF CaO particles with SO$_2$ is increased by a factor of $5 \times 10^2 - 5 \times 10^3$ in comparison with that obtained by conventional dry processes which use CaO particles with a diameter greater than 1 μm. Our results strongly support the hypothesis that application of UF CaO particles to the conventional dry injection process could significantly increase SO$_2$ removal efficiency.

Several studies have been directed at investigating the reaction rate of SO$_2$ with CaO particles having dp > 1 μm[1-6, 10, 11]. In fact it is generally known that over 100 sec is required to achieve 70 % conversion of CaO, which is too long compared with the available residence time in a boiler furnace.

1. Experimental

Figure 1 shows the experimental apparatus for UF particle formation, where the UF CaO particles are generated by directing a Nd: YAG laser beam (1064 nm) onto a rotating rod of either Ca (OH)$_2$ (Kuzuu-slaked lime; rod

1) or CaCO$_3$ (Chichibu limestone; rod 2). **Table 1** summarizes their chemical compositions. The generated particles are transported by carrier air to a quartz reactor (i.d., 24 mm; length, 450 mm) where they react with a gas mixture of SO$_2$ and N$_2$. The mixed gas flow rate was 0.3 l/min and that of the carrier air was 1.8 l/min. Electric heaters controlled the reaction temperature from 973 to 1273 K. The initial SO$_2$ concentration before reaction with UF particles was measured as 220 ppm by an infrared (IR) absorption SO$_2$ analyzer. The reaction gas at each reaction temperature was water-cooled in the downstream region to about room temperature. The particles were collected in a silica fiber filter and the outlet SO$_2$ concentration was measured as mentioned above, with the particle concentration being subsequently calculated by accurately weighing the filter/collected particles. An inductively coupled plasma (ICP) analyzer measured the amount of fixed sulfur in order to estimate the conversion of CaO to CaSO$_4$.

2. Results and Discussion

Transmission electron microscopy (TEM) was utilized to observe the UF CaO particles. **Figure 2** shows the particles formed from rod 2 (CaCO$_3$). Their number median diameter (NMD) was estimated by the particle size distribution of TEM photos to be about 17 nm and the surface mean diameter (SMD) as about 26.6 nm. The particles' specific surface area (σ_g) was calculated from the SMD to be 66.9 m^2/g, whereas when using the BET absorption method it was 53 m^2/g. This implies that σ_g is mainly determined by the external surface area of the primary particles. Similar results were obtained for rod 1.

**Figure 3** shows x-ray diffraction (XRD) patterns of UF particles formed from rods 1 and 2, where both indi-
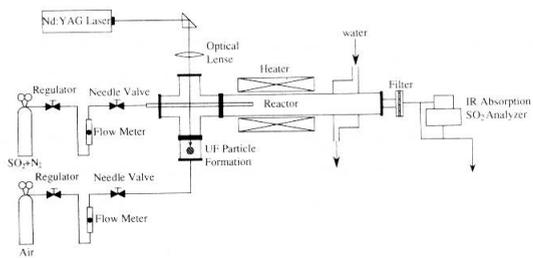
Fig. 1 Schematic of experimental apparatus for UF particle formation

Table 1. Chemical Composition of Kuzuu-slaked lime $(Ca(OH)_2)$ and Chichibu limestone $(CaCO_3)$

Constituent	Kuzuu Slaked lime rod 1 (wt%)	Chichibu Limestone rod 2 (wt%)
Ignition-loss	28.19	42.51
CaO	66.52	55.49
MgO	4.14	0.91
CO_2	3.61	-
SiO_2	0.18	0.29
Fe_2O_3	0.04	0.07
Al_2O_3	0.07	0.08
P	-	-
S	-	-
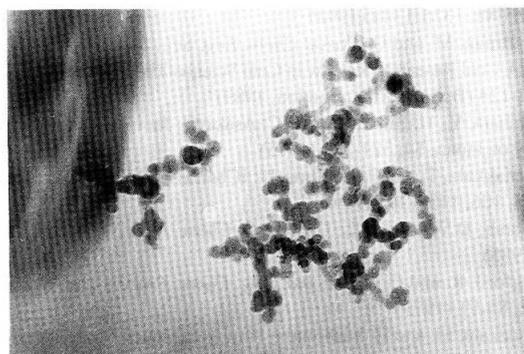
100 nm

Fig. 2 TEM photo of UF CaO particles formed from rod 2 $(CaCO_3)$

Fig. 3 XRD patterns of UF particles formed from (a) rod 1, $Ca(OH)_2$ and (b) rod 2, $CaCO_3$

Particle	dp (μm)	σ g (m²/g)	Reference
UF : ●	17×10^{-3}	53	Present
A : △	44-63	0.66	Present
B : ○	1	3.0	2
C : □	4	-	3
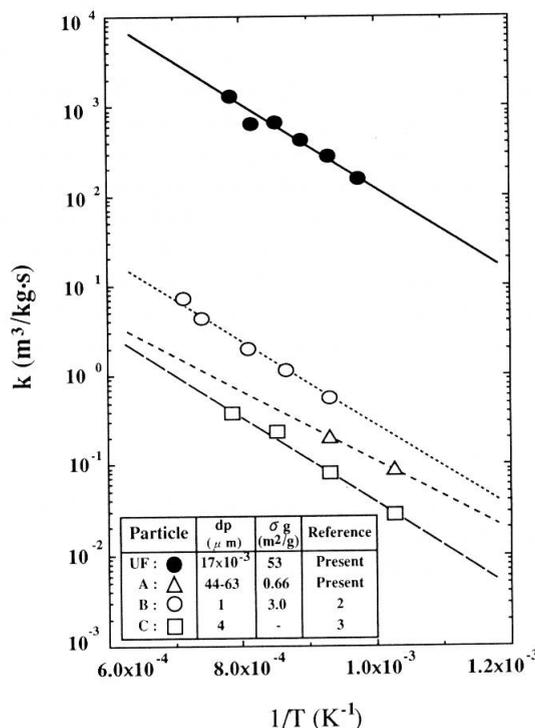
Fig. 4 Reaction rate of CaO with SO_2 versus inverse temperature for various particle sizes

cate that CaO is the main constituent, and consequently, Ca $(OH)_2$ and $CaCO_3$ are believed to have been converted to CaO by the high-temperature plasma induced by laser ablation.

The desulfurization reaction rate was measured on the basis of the SO_2 gas phase under various reaction temperatures, and the reaction rates per unit mass were calculated from these data. Several definitions exist for the reaction rate and reaction rate constant (k), although the reaction rate based on unit mass of solid (r) is normally applied since the desulfurization process should obtain a maximum desulfurization rate with a minimum weight of injected limestone. Here, r, for solid CaO is defined as:

r = moles CaO reacted/(unit mass of solid)·(time)

Because r is proportional to the SO_2 concentration, the first order equation is

$r = k\,C_{SO_2}$ [moles/kg·s]

To provide a comparative evaluation, the reaction rate of SO_2 with ordinary-size CaO particles (dp = 44-63 μm) was also measured using a fixed bed reactor in which CaO particles were dispersed within the inert particles packed in the quartz tube (*i.d.*, 5 mm). A mixed gas (SO_2, 1000 ppm; N_2, balance) was premixed with air and flowed through the reactor at 2.0 std l/min. **Figure 4** shows a plot of k versus 1/T for these results, as well as those by Borgwardt *et al.*[2] and Gopalakrishnan *et al.*[3] at a dp of 1 and 4 μm, respectively. Note that r for the UF particle was 5

$\times 10^2$-5 $\times 10^3$ times greater than that for the other CaO particles larger than 1 μm. This exceptionally high r value is considered to be caused by differences in σ_g, i.e., for particle A, σ_g is 0.66 m^2/g, whereas σ_g is 53 m^2/g for the UF particle.

However, r is not solely determined by σ_g as demonstrated by the behavior of particle B, where σ_g is only one-tenth the value of the UF particle. These results indicate that for the case of ordinary-size CaO particles, the entire pore surface could not be used for the reaction due to the blockage of the micro-pore by the formed CaSO$_4$.

The laser ablation method we employed for generating UF CaO particles was used for experimental convenience. It is realized that large-scale application of this method would not be suitable for developing countries due to its high cost. For scale-up purposes, the arc-plasma torch method can instead be applied to generate the necessary UF particles. One recent experiment using a small-scale arc plasma showed that UF CaO particles could be produced by the plasma method. The results will be published elsewhere. In addition, a recycle system could be incorporated into the desulfurization process, such that 90 % of CaO particles could be returned to the furnace after desulfurization of recovered CaSO$_4$ UF particles. By implementing these two ideas, we estimate that 2 MW will be needed to produce the required quantity of UF CaO particles for a conventional size, 200-MW power generating station, i.e., about 1 % the total electrical output. In fact, if our process was applied in a to-be-built, 200-MW coal combustion burner, based on previous estimates[13], the annual cost would be 50 % less that of the semi-dry desulfurization method[9], the most economical process used to date.

Conclusion

Ultrafine CaO particles were produced by laser ablation method using a Nd: YAG laser. The reaction rate of ultrafine CaO particles with SO$_2$ was examined. It was found that the reaction rate of ultrafine CaO particles with SO$_2$ was 5 $\times 10^2$ – 5 $\times 10^3$ times higher than that for the other CaO particles larger than 1 μm which have been used in the conventional dry processes. These results show that application of ultrafine CaO particles to conventional dry injection process can significantly increase SO$_2$ removal efficiency.

Nomenclature

d_p	= diameter	[μm]
σ_g	= specific surface area	[m^2/g]
k	= reaction rate constant	[m^3/kg.s]
r	= reaction rate	[moles/kg.s]
T	= temperature	[K]

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