EFFECTS OF SALTS ON LIMESTONE DISSOLUTION RATE IN WET LIMESTONE FLUE GAS DESULFURIZATION

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Introduction

In the wet limestone flue gas desulfurization (FGD) process, powdered limestone dissolves and neutralizes acidity produced by SO_2 absorption in the liquid phase. It is known that the soluble salts have effects[2, 4] on the dissolution rate of the limestone used as the absorbent, but sufficient quantitative examinations had not yet been conducted to clarify the phenomena. In this study, limestone slurries, each containing a single salt, were titrated with sulfuric acid to measure the dissolution rate. The dissolution rates of limestone in mixed salts were also examined in detail since various salts exist in mixed states in commercial FGD processes.
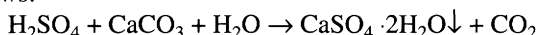
1. Experimental

In the so called "*in-situ* oxidation[1]" limestone desulfurization process, limestone particles dissolve into the aqueous phase of the slurry and react with the SO_4^{2-} ion.

The dissolution rate of the limestone was measured in the batch reactor shown in **Fig. 1.**

The experiment was initiated by the addition of 20g of limestone and 200g of seed gypsum.

A sulfuric acid solution (1.0 mol/l) was titrated into a limestone slurry of 2l in the reactor to maintain the pH at 5.2 ±0.1.

The titrated sulfuric acid dissolves limestone as follows:

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O\downarrow + CO_2$$

The mass balance equation of SO_4^{2-} for the titration is given by

$$F \cdot C_s \cdot dt = r \cdot V \cdot dt + V \cdot dC + C \cdot dV \qquad (1)$$

Where F is the titration speed of H_2SO_4 [l/h], Cs is the concentration of H_2SO_4 [mol/l], t is time [h], r is the dissolution rate of limestone with H_2SO_4 [mol/l·h], which is thought to express the removal rate of SO_4^{2-} by gypsum crystallization, V is the volume of limestone slurry in the reactor [l] and C is the concentration of H_2SO_4 in the slurry [mol/l].

In this work, the volume change of slurry was small and the steady state of SO_4^{2-} concentration in slurry was attained due to the prevention of supersaturation by addition of the seed gypsum. Thus, the limestone dissolution rate was expressed by

$$r \cong \frac{F \cdot Cs}{V} \qquad (2)$$

Here, because the limestone dissolution rate (r) varies with particle size distribution and chemical composition, limestone with a consistent particle size distribution (45 μm, 97.2 wt% passing, 97.5 wt% purity) was used throughout the experiments to eliminate this source of variability.

As the comparison standard, the limestone dissolution rate when 70% of initially charged limestone dissolves was employed.

2. Results and Discussion

Figure 2 shows the relationship between concentrations of various coexisting salts and the relative dissolution rates (R) of limestone. R is the ratio of the dissolution rate (r_0) in a standard solution containing no salt and the dissolution rate (r) in a solution containing a salt, and is defined by

$$R = \frac{r}{r_o} \qquad (3)$$

In chloride solutions such as $CaCl_2$, $MgCl_2$ and $NaCl$, the dissolution rate decreases with the concentration of salt.

When sulfates such as Na_2SO_4 and $MgSO_4$ were added, the dissolution rate increased. The effects of the sulfates were entirely different from those of the chlorides.

Figure 3 (a) shows how the dissolution rate of limestone changed in the solution containing Na_2SO_4 at different mixing ratios. With a greater mixing ratio of Na_2SO_4, the dissolution rate increased in both the Na_2SO_4–$MgSO_4$ and Na_2SO_4–$NaCl$ systems.
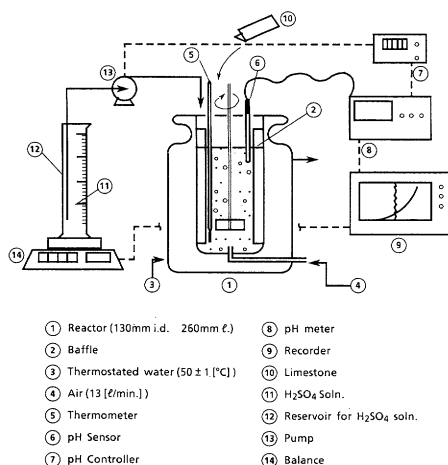
Figure 3 (b) expresses the dissolution rate as a
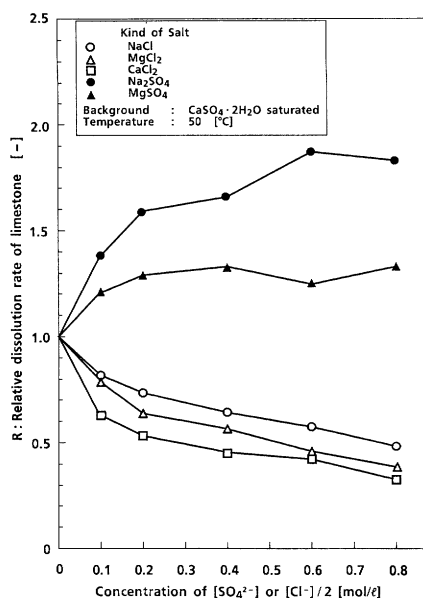
Fig. 1 Limestone dissolution rate measurement apparatus

① Reactor (130 mm i.d. 260 mm ℓ.)	⑧ pH meter
② Baffle	⑨ Recorder
③ Thermostated water (50 ± 1 [°C])	⑩ Limestone
④ Air (13 [ℓ/min.])	⑪ H₂SO₄ Soln.
⑤ Thermometer	⑫ Reservoir for H₂SO₄ soln.
⑥ pH Sensor	⑬ Pump
⑦ pH Controller	⑭ Balance

Fig. 2 Effect of salt concentration on limestone dissolution rate

Fig. 3 (a) Limestone dissolution rate in mixed salts solution

Fig. 3 (b) Limestone dissolution rate in mixed salts solution

function of the $MgCl_2$ mixing ratio in both the $MgCl_2$–$MgSO_4$ and $MgCl_2$–$CaCl_2$ systems.

Similarly to the case in Fig. 3 (a), the effects of the mixed salts on the dissolution rate were located midway between the effects of these salts when they were added alone.

To explain these results qualitatively, the authors assumed the following influencing factors.

a) The dissolution rate decreases when the ionic strength increases as observed in a chloride solution.

b) The increase of the dissolution rate in a sulfate solution is brought about by the effect of bisulfate ions coexisting in the solution in equilibrium.

Factor a) is based on the previous report[3] that the dissolution of limestone is controlled primarily by the diffusion of H^+ from the bulk of solution of the limestone surface, and high ionic strength inhibits the dissolution by decreasing the diffusivity of the H^+.
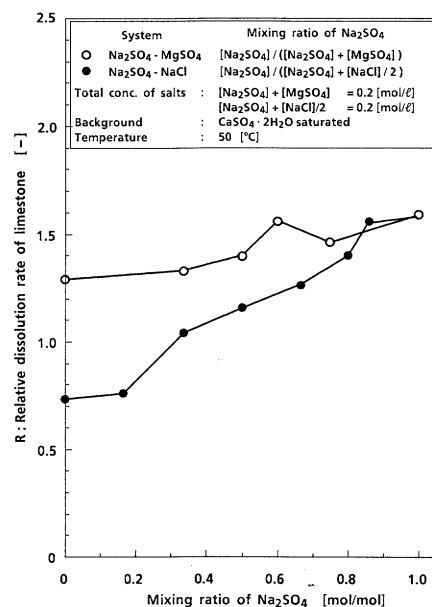
Factor b) is due to the idea that sulfates enhance the dissolution rate by providing an additional means of diffusing acidity, i.e. the bisulfate ion, to the limestone surface.

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