

COMMUNICATION

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KINETIC BEHAVIOUR OF LIME SLURRIES
IN FLUE-GAS DESULFURIZATION PROCESSES

1. INTRODUCTION

Sulfur dioxide is removed from flue gases of coal fired power plants in various commercial processes. At present, the lime and limestone flue gas desulfurization (FGD) processes are the most advanced of the throw away FGD systems [1]-[4]. In these systems sulfur dioxide is removed from flue gas and converted to calcium sulfite or/and calcium sulfate sludge. A calcium sulfite-calcium sulfate sludge is usually produced in natural oxidation systems, while forced oxidation systems produce primarily calcium sulfate sludges.

The kinetics of chemical reaction which produces these solids and the solids' respective physical characteristics are specially important in designing and operating FGD systems. The rate at which calcium sulfite and/or calcium sulfate precipitates is important in controlling scaling on scrubber surfaces and in designing reaction tanks [5], [6]. Precipitation rates are also important in determining particle size distribution of the respective sulfur sludge. Particle size distribution has been shown to be a major factor affecting the settling and dewatering properties of calcium sulfite and calcium sulfate sludges.

The poor dewatering properties of calcium sulfite and, to a lesser extent, calcium sulfate are well documented and are responsible for most of the problems associated with sludge disposal in FGD systems.

From a chemical engineering viewpoint, many published works [7]-[16] deal with the modelling of the diffusion of sulfur dioxide, which is considered to be the controlling step in the slurry system; in some of them, the influence of addition of foreign substances such as chlorides, sulfates, carbonates, etc, on the absorption rate [4], [10] has also been reported, but very little has been said about the kinetics of the chemical reaction, which on the other hand could exert an important influence on the process.

In this work the kinetics of the formation of calcium sulfite in a continuous slurry system containing absorbed sulfur dioxide (H_2SO_3) and dissolved calcium hydroxide is reported. Two different kinetic models have been able to fit the experimental results depending on the concentration of sulfur dioxide: nucleation models for low concentrations of sulfur dioxide and growth models for results obtained at higher concentrations of sulfur dioxide [17].

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2. EXPERIMENTAL

Experiments at different initial concentrations of aqueous sulfur dioxide and calcium hydroxide were performed isothermally in a continuous stirred tank reactor (CSTR). Calcium hydroxide solution was stored in a 25 dm³ bottle under a carbon dioxide free atmosphere. Initially all the inlets to the storage bottle were closed and vacuum was applied. After distilled water was added to the filtration unit and allowed to flow into the storage bottle, the supernatant solution of the calcium hydroxide slurry was added to the filtration unit. The vacuum was then released to the atmosphere [18]. Absorbed sulfur dioxide was stored into a similar 25 dm³ bottle. Controlled amounts of both solutions were allowed to flow (using rotameters as control instruments) into the CSTR.

The sulfite ion concentration in the outlet solution was determined by iodometric titration after filtration of the samples and separation of the residual solid (CaSO₃). The experiments were carried out at a temperature of 20°C ± 1°C.

3. RESULTS AND INTERPRETATION

Two different types of experiments were performed: experiments at various concentrations of calcium hydroxide ($2.5 \times 10^{-3} \text{ M} \leq \text{Ca(OH)}_2 \leq 2 \times 10^{-2} \text{ M}$) and constant concentration of sulfurous acid ($8 \times 10^{-3} \text{ M}$), and experiments at different concentrations of sulfurous acid ($5 \times 10^{-3} \text{ M} \leq \text{H}_2\text{SO}_3 \leq 1 \times 10^{-2} \text{ M}$) and constant concentration of calcium hydroxide ($1 \times 10^{-2} \text{ M}$).

In order to apply a differential method, reaction rates were calculated from the outlet concentration C and mean residence time τ :

$$r = \frac{C_0 - C}{\tau}$$

Reaction rate curves are shown in figures 1 and 2 against outlet concentration of sulfurous acid. Continuously increasing curves have been fitted to potential expressions

$$r = K_c \cdot C_0^n (1-x)^n,$$

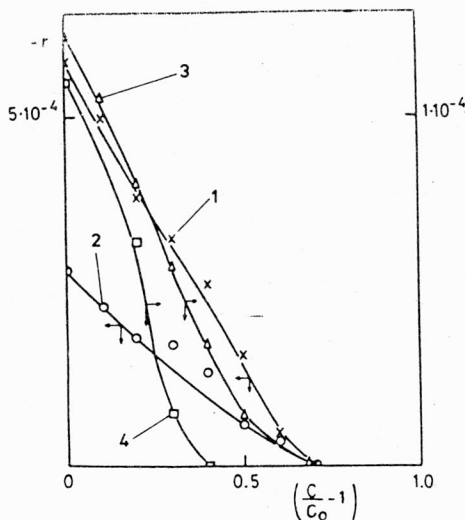


Fig. 1. Reaction rates versus outlet constant concentration of H₂SO₃, i.e., $8 \times 10^{-3} \text{ M}$, and various concentrations of Ca(OH)₂: 1 - $2 \times 10^{-2} \text{ M}$, 2 - 10^{-2} M , 3 - $7.5 \times 10^{-3} \text{ M}$, 4 - $2.5 \times 10^{-3} \text{ M}$

r being the solid formation rate, n the potential kinetic order ($n = 0, 1, 2$ etc), x the conversion and K_c the kinetic constant [17]. Reaction rate curves with a maximum have been fitted to the following expression, usually given for nucleation:

$$x = K_c(1-x)\exp(I/\tau),$$

where I is the incubation period of nucleation which varies depending on the experimental conditions [17].

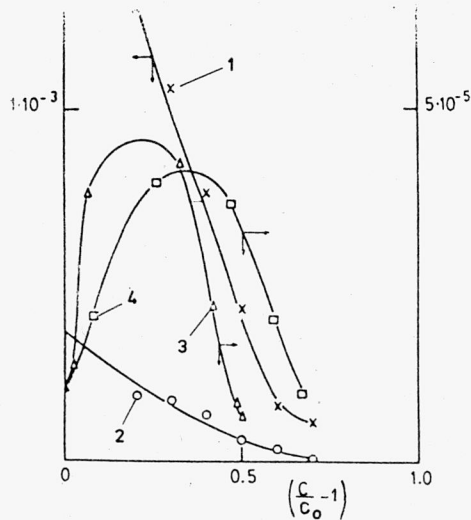


Fig. 2. Reaction rates versus outlet constant concentration of $\text{Ca}(\text{OH})_2$, i.e., 10^{-2} M, and various concentrations of H_2SO_3 : 1 - 10^{-2} M, 2 - 8×10^{-3} M, 3 - 6×10^{-3} M, 4 - 5×10^{-3} M

4. CONCLUSIONS

The kinetics of formation of calcium sulfite in a slurry reactor has been studied. Two different kinetic models, i.e., one corresponding to a growth controlling mechanism (potential law) and the second corresponding to a nucleation controlling mechanism have been able to fit the experimental results depending on the experimental conditions. These models are useful in the design and operation of the flue gas desulfurization systems by the wet process.

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