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Kinetic study of the reaction between sulfur dioxide and calcium hydroxide at low temperature in a fixed-bed reactor

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Abstract

A quantitative study of the influence of inlet sulfur dioxide concentration (600–3000 ppm), relative humidity (20–60%), reactor temperature (56–86°C) and different amounts (0–30 wt.%) of inorganic additives (NaCl, CaCl₂ and NaOH) on gas desulfurization has been carried out in a continuous downflow fixed-bed reactor containing calcium hydroxide diluted with silica sand. Results show that the reaction rate does not depend on sulfur dioxide partial pressure (zero-order kinetics) and that the temperature and the relative humidity have a positive influence on reaction rate. An apparent activation energy of 32 kJ/mol Ca(OH)₂ has been estimated for the reaction.

An empirical reaction rate equation at 71.5°C and 36.7% relative humidity that includes the type and amount of additive is proposed. It has been found that calcium chloride is the best additive studied because it allows for a higher degree of sulfur dioxide removal. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Desulfurization; Sulfur dioxide; Calcium hydroxide; Kinetics; Inorganic additives

Abbreviations: HR, relative humidity, %; k , kinetic rate constant for calcium hydroxide without additives, mol/h mol OH⁻; k_{ad} , kinetic rate constant for calcium hydroxide–additive mixture, mol/h mol OH⁻; k' , kinetic rate constant defined by Eq. (3), mol/h mol OH⁻; n , reaction order for relative humidity, dimensionless; m , reaction order for the weight ratio of additive, dimensionless; mLN, normal milliliters (temperature of 0°C and atmospheric pressure); r , reaction rate, mol SO₂/h mol OH⁻; w_{ad} , weight ratio of additive, dimensionless

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1. Introduction

The increasing concern during the last few years on the protection of the environment has had its influence on the design and operation of power plants, especially on the reduction of sulfur dioxide and nitrogen oxide emissions from them. They are the main pollutants from coal and fuel-oil combustion in power plants. Both gases are responsible for acid rain.

In USA and Europe, new power plants that use fuels with significant quantities of sulfur have to meet severe standards to reduce these air pollutants. One of the major problems facing older power plants is that they were designed prior to the present standards for pollution control and therefore have no facilities on space to incorporate such controls.

The technologies to control sulfur dioxide emissions can be distributed into three groups by considering if the treatment is done before, during or after the combustion. It seems clear that the last group of technologies cited is the most advantageous, from various points of view, for power stations which have been in operation for many years. These are called FGD technologies (Flue Gas Desulfurization), and among them, the most used [3,11] are: IDS (In-Duct Scrubbing, developed by General Electric); E-SO_x (developed by US EPA, Babcock and Wilcox, Ohio Coal Development Office and Ohio Edison), EPRI HYPAS (Hybrid Pollution Abatement System, developed by Electric Power Research Institute), DRAVO HALT (Hydrate Addition at Low Temperature, developed by Dravo), CONSOL COOLSIDE (developed by Consolidated Coal Company) and ADVACATE (developed by Acurex and US EPA). These processes are based on the injection of a solid sorbent plus water by spraying or injecting a slurry into the duct situated between the air preheater and the particulate collection system. Calcium hydroxide or limestone are usually used as sorbents to capture sulfur dioxide and a calcium sulfite/sulfate mixture is obtained as the reaction product.

Klingspor et al. [9] and Strömberg [16] proposed a mechanism to explain the reaction between sulfur dioxide and calcium hydroxide or calcium carbonate in the presence of water vapor. According to them, when the relative humidity is low (below 20%), sulfur dioxide and water can be adsorbed on the solid surface, however, no reaction occurs until there is at least a monolayer of water molecules adsorbed on the surface. As the relative humidity increases, less sulfur dioxide can be adsorbed on the surface because water adsorption on the solid occurs preferentially due to intermolecular forces. Thus, sulfur dioxide has to be absorbed on the adsorbed water, forming complexes where the sulfur atom is bound to the oxygen atom of water. This fact leads to the formation of a positive charged hydrogen atom that can combine with hydroxide or carbonate ions from the sorbent to form reaction intermediates and products. Experimental findings show that the reaction rates for lime and limestone are similar. Consequently, the complex formation SO₂nH₂O is considered to be the rate-determining step, since all further reactions are different for the two types of sorbents. The initial rate of the process is independent of sulfur dioxide concentration when the relative humidity is below 70%. Above this value, the reaction rate becomes gradually more and more dependent on the sulfur dioxide partial pressure. This fact can be attributed to the formation of stable configurations of water ligands around the sulfur dioxide molecules. Also, it has been

found that the initial reaction rate is a very weak function of temperature but increases exponentially with relative humidity, for both hydrated lime and limestone.

Jorgensen et al. [7] also studied this reaction in a bench-scale sand bed reactor. Some of their conclusions point out that the calcium hydroxide conversion has a very strong dependence on relative humidity. The conversion rate is increased moderately with temperature in agreement with activation energy of 25 kJ/mol. However, there is no clear indication of increasing conversion with increasing sulfur dioxide concentration.

Ruiz-Alsop and Rochelle [14] found that the relative humidity is the most important variable affecting the reaction of sulfur dioxide and calcium hydroxide. The chemical reaction taking place at the surface of the unreacted calcium hydroxide presents zero-order kinetics in sulfur dioxide. At high relative humidity and/or high SO₂ concentration, the chemical reaction at the surface of the unreacted calcium hydroxide solid controls the overall reaction rate. At low relative humidity and/or low sulfur dioxide levels, diffusion of sulfur dioxide through the solid product layer becomes the rate-controlling step. The reaction rate has a weak temperature dependence. The activation energy of the reaction was estimated to be 12 kJ/mol.

Experimental data by Krammer et al. [10] showed that the reaction rate depends on the sulfur dioxide concentration but only at low concentrations and not so obvious at higher concentrations. In contrast to other publications, they found that the influence of SO₂ concentration on the reaction rate is rather linked to the conversion than to the relative humidity, which has a major impact on the conversion throughout the entire reaction as usually reported in literature. But they found out that the initial reaction rate seems to be independent of relative humidity and sulfur dioxide concentration, which had not been reported yet. They postulated that the reaction can be divided into the following four steps. (1) During the initial stage, a chemisorption process of the sulfur dioxide on the particle surface seems to be important and the reaction rate decreases exponentially with increasing conversion. (2) Simultaneously, a nucleation process dominates the formation of the consecutive product layers where the reaction rate increases with increasing relative humidity. (3) The rate of reaction increases until product layer diffusion takes over and reaction rate decreases again with conversion. It should be noted that only relative humidity has an impact on product layer diffusion. (4) Beyond a conversion of around 9%, reaction rate drops significantly, which can be due to pore closure.

Irabien et al. [5] consider the adsorption of sulfur dioxide on calcium hydroxide acting as a nonideal solid sorbent is the rate-limiting step. They use a parameter referring to this nonideal behavior of the solid surface as independent of temperature but exponentially dependent on relative humidity. The authors obtained activation energy of 75 kJ/mol for the reaction.

All published work thus far indicates that relative humidity has the greatest impact on the reaction rate between sulfur dioxide and calcium hydroxide. The relative humidity is in turn correlated with the moisture content of the solids. Additives that will modify the moisture content of the calcium hydroxide solids in equilibrium with a gas phase of a given relative humidity would then be expected to enhance the reactivity of calcium hydroxide towards sulfur dioxide in FGD processes.

Organic and inorganic additives have been tested in spray dryer systems to improve the desulfurization power of calcium hydroxide and calcium carbonate [1,2,4,7,8,12–15]. It seems that inorganic hygroscopic salts such as barium, potassium, sodium and calcium chlorides and also cobalt, sodium and calcium nitrates would be the most effective ones. Some researchers also consider sodium hydroxide as an effective additive due to its alkaline and hygroscopic properties.

Ruiz-Alsop and Rochelle [14] indicated that deliquescence alone does not explain the positive effect of some salts. They contend that for an additive to be effective, it is also necessary that the hydroxide of the cation be very soluble, otherwise, the cation will precipitate out as the hydroxide and the anion will form the calcium salt which could not be hygroscopic. The effectiveness of a certain salt also depends on the relative humidity. This could be expected because when the relative humidity of the gaseous phase is lower than the water activity in a saturated solution of the salt, it would not absorb water and so, it would not enhance the calcium hydroxide reactivity. These researchers contend that chlorides and sodium nitrate modify the properties of the product (half-hydrated calcium sulfite) layer that is formed as the reaction takes place, thereby facilitating the access of sulfur dioxide to unreacted calcium hydroxide, which remains in the interior of the particle.

The scope of the present work is to quantify the influence on the reaction rate of sulfur dioxide concentration, relative humidity, temperature and type and amount of additive. An empirical equation, which relates the reaction rate with these variables, has been obtained and an apparent activation energy value for the reaction has also been determined from kinetic constants at different temperatures by using the Arrhenius plot.

2. Experimental section

This study was carried out in an experimental setup shown in Fig. 1. This equipment consists of a continuous feeding and humidification system of a gaseous stream, a fixed-bed reactor and an analytical system [6]. The apparatus is operated with a personal computer using LabView software (National Instruments), which allows programming and control of the experimental conditions, namely, nitrogen and sulfur dioxide flow rates, humidification temperature and electric resistance heating of the pipes to avoid condensations and also provides the experimental data acquisition, in particular nitrogen and sulfur dioxide flow rates, reaction temperature, pressure, relative humidity and sulfur dioxide concentration, vs. reaction time.

Simulated flue gas was obtained by mixing sulfur dioxide and nitrogen from separate cylinders in appropriate amounts using mass flow controllers (MF SO₂ and MF N₂ in Fig. 1) were supplied by Brooks Instrument, Veenendaal). Before mixing, pure nitrogen was passed (by switching on valve 1 from the computer) through the humidification system (H.S. in Fig. 1) that consisted of three cylindrical flasks with 200 ml of water each submerged into a thermostatic bath. Each flask contains small glass spheres to improve the contact between gas and water. After the humidification system, the temperature and the relative humidity of the wet nitrogen were measured by using a Vaisala HMP 235 transmitter (H.T. in Fig. 1). At the same location, the pressure was

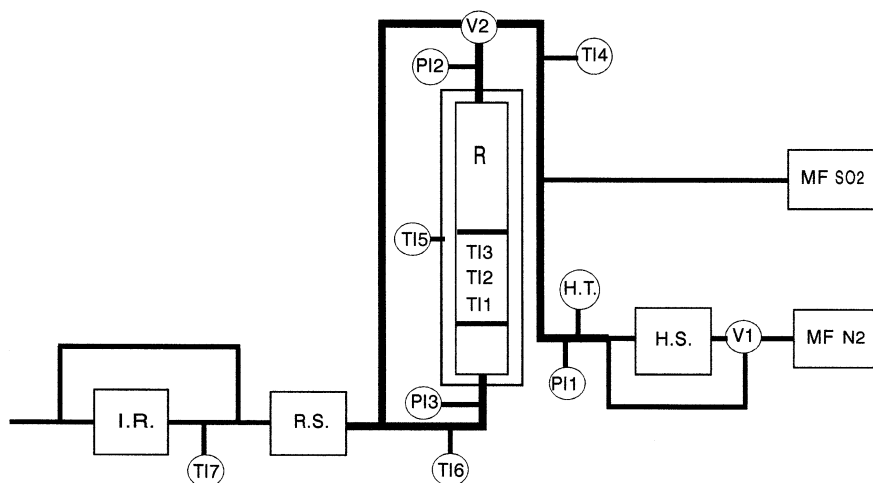


Fig. 1. Schematic diagram of desulfurization apparatus. H.S.: humidification system; H.T.: humidity transmitter; R: downflow fixed-bed reactor; R.S.: refrigeration system; I.R.: sulfur dioxide analyser.

also measured (PI1 in Fig. 1) to calculate the flow rate of water vapour generated. The wet nitrogen by-passed the reactor until the desired experimental conditions were reached and then valve 2 was opened from the computer to allow the gaseous stream flow through the reactor. The bed was always humidified for 15 min while the sulfur dioxide analyser was set to zero. At this time, the desired flow of sulfur dioxide was introduced by a mass flow controller and the experiment began. Data generated during the experiment were stored in an EXCEL format computer file.

The glass reactor, a jacketed Pyrex tube (450 mm height, 12 mm i.d.) with a porous plate to hold 1 g of dry calcium hydroxide (Probus, 99% purity and particle size smaller than 0.05 mm in diameter) or calcium hydroxide–additive mixtures (all additives were supplied by Fluka, 99% purity and particle size smaller than 0.05 mm in diameter) diluted with 8 g of silica sand (Merck; 0.1–0.3 mm in diameter) to assure isothermal operation and to prevent channelling due to excessive pressure drop, was thermostated by pumping a thermal fluid (water–ethyleneglycol mixture) from an external thermostatic bath.

The reacted flue gas is passed through a refrigeration system (R.S. in Fig. 1) in order to remove water because it interferes with the SO_2 analyser measurement (infrared non-dispersive Rotork 411; I.R. in Fig. 1). The output from the analyser was continuously collected by the computer for 1 h (experiment time) and the concentration (ppm) of sulfur dioxide stored as a function of time (experimental curve). Each experiment was conducted in the same manner except a reactive solid was substituted for the 10 g of inert silica (“blank” experiment) to obtain a reference flow curve. The reaction rate was calculated as SO_2 mol removed/h mol OH^- from the area enclosed by the two curves (experimental and “blank”). Some experiments were replicated to estimate the experimental error in reaction rate.

3. Results and discussion

3.1. Influence of sulfur dioxide concentration

To test the influence of sulfur dioxide partial pressure on reaction rate, twelve experiments were performed at the following conditions: reactor temperature: 71.5°C; relative humidity in the reactor: 38%; nitrogen flow rate: 1500 mLN/min; sulfur dioxide flow rates: 1, 2, 3, 4 (repeated three times to evaluate the experimental error) and 5 mLN/min. The sorbent was 1.0 g of dry calcium hydroxide mixed with 8.0 g of silica sand. Five “blank” experiments were made at the same conditions to obtain the influence of flow model due to the five different flow rates of sulfur dioxide used.

The reaction rate values obtained for the different flow rates of sulfur dioxide are summarised in Table 1. Taking into account the reaction rate values for the three duplicate runs, the experimental error in the reaction rate was ± 0.0043 mol SO₂/h mol OH⁻ (5.6% relative error). As a consequence, it can be deduced that reaction rate between sulfur dioxide and calcium hydroxide does not depend on sulfur dioxide partial pressure for sulfur dioxide concentration less than 3000 ppm. This conclusion is similar to that found by other researchers mentioned in the Introduction section.

3.2. Influence of temperature and relative humidity

A set of experiments was performed to evaluate simultaneously the influence of temperature and relative humidity on reaction rate. In all experiments, flow rates for nitrogen and sulfur dioxide were 1500 and 4 mLN/min, respectively. A total of 1.0 g of calcium hydroxide diluted into 8.0 g of silica sand was used.

Twelve “blank” experiments were performed at the same temperatures and relative humidities. The sulfur dioxide concentration vs. time curves were the same within the limits of experimental error. Thus, is verified that no reaction takes place between sulfur dioxide and silica sand and that relative humidity and temperature do not influence the flow model significantly.

Table 2 summarises the reaction rates obtained as a function of temperature and relative humidity. From the three duplicate runs at 56.5°C and 49% average relative humidity, the experimental error in reaction rate was calculated and a value, ± 0.0041

Table 1

Reaction rates obtained without additives for different flow rates and partial pressures of sulfur dioxide at 71.5°C and 38% relative humidity

| SO ₂ flow rate (mLN/min) | SO ₂ partial pressure (atm) | Reaction rate, <i>r</i> (mol SO ₂ /h mol OH ⁻) |
|-------------------------------------|--|---|
| 1 | 0.0008 | 0.0762 |
| 2 | 0.0016 | 0.0705 |
| 3 | 0.0024 | 0.0753 |
| 4 | 0.0031 | 0.0799 |
| 4 | 0.0032 | 0.0721 |
| 4 | 0.0033 | 0.0793 |
| 5 | 0.0040 | 0.0707 |

Table 2

Reaction rates obtained without additives at different temperatures and relative humidities

| Temperature (°C) | Relative humidity (%) | Reaction rate, r (mol SO ₂ /h mol OH ⁻) |
|------------------|-----------------------|--|
| 56.5 | 39.9 | 0.0573 |
| 56.5 | 48.3 | 0.0753 |
| 56.5 | 49.9 | 0.0737 |
| 56.5 | 49.1 | 0.0676 |
| 56.5 | 60.4 | 0.1144 |
| 71.5 | 20.5 | 0.0487 |
| 71.5 | 38.2 | 0.0799 |
| 71.5 | 36.2 | 0.0793 |
| 71.5 | 40.3 | 0.0721 |
| 71.5 | 56.5 | 0.1316 |
| 86.2 | 20.1 | 0.0456 |
| 86.2 | 31.5 | 0.0782 |
| 86.2 | 47.3 | 0.1241 |

mol SO₂/h mol OH⁻ (5.7% relative error), similar to the previous one, was obtained. This indicates that the experimental error in reaction rate is of the same order for the range considered.

As a general rule, it can be clearly affirmed that at constant temperature, the higher the relative humidity, the higher the reaction rate. When experiments done at similar relative humidity but at different temperatures are compared, it can be seen that the reaction rate increases with temperature.

To assess the quantitative influence of both variables on reaction rate, which is the controlling step at high relative humidity [14] and taking into account that there is no influence of sulfur dioxide concentration on reaction rate, data were fitted to the empirical equation:

$$r = k(\text{HR})^n \quad (1)$$

where k is the kinetic rate constant and n is the kinetic order with respect to relative humidity in percent. The best fit led to the following values of the rate constant: 7.49×10^{-4} mol/h mol OH⁻ at 56.5°C; 1.03×10^{-3} mol/h mol OH⁻ at 71.5°C and 1.21×10^{-3} mol/h mol OH⁻ at 86.2°C. The empirical reaction order for the relative humidity was evaluated as $n = 1.2$.

Assuming that the temperature dependence of the kinetic rate constant follows the Arrhenius law, a good fit was obtained with an apparent activation energy of 32 kJ/mol Ca(OH)₂. This value is somewhat higher than the one obtained by Ruiz-Alsop and Rochelle [14], but much lower than the reported value by Irabien et al. [5].

3.3. Influence of the type and amount of additives

Sodium chloride, calcium chloride and sodium hydroxide were tested as additives to enhance the reactivity of calcium hydroxide towards sulfur dioxide. The experiments were performed at 71.5°C and 36.7% of relative humidity. Flow rates of nitrogen and

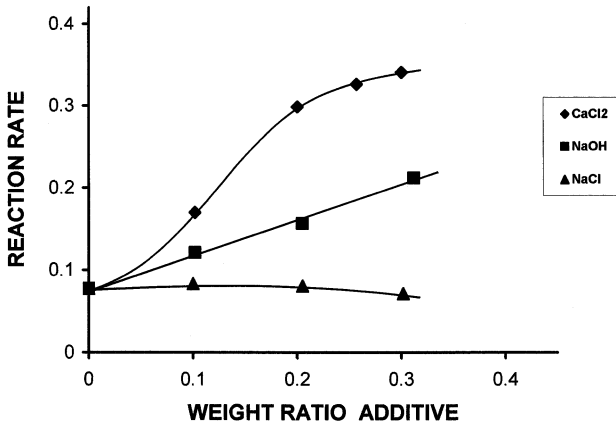


Fig. 2. Reaction rates vs. weight ratio of additives at 71.5°C and 36.7% relative humidity. (◆) CaCl₂; (■) NaOH; (▲) NaCl.

sulfur dioxide were 1500 and 4 mL/min, respectively. The amount of additives ranged from 10 to 31.2 wt.%.

Fig. 2 shows the reaction rate values as a function of the amount of the three additives used. As can be seen, the reaction rate increases with increasing concentration of calcium chloride and sodium hydroxide. Surprisingly, calcium chloride was found to be more effective than sodium hydroxide, which is counter intuitive, since CaCl₂ has poor alkaline and hygroscopic properties. Since calcium chloride is a deliquescent salt, one must conclude that deliquescence is a desirable property for sulfur dioxide removal.

Upon testing, no significant enhancement on reaction rate was found when different amounts of sodium chloride were used. It seems that its hygroscopic character is not enough to improve significantly the desulfurization power of calcium hydroxide.

As Ruiz-Alsop and Rochelle [14] reported, the presence of additives affects the kinetic rate constant. With increasing amounts of the same additive, the kinetic rate constant increased linearly. To know the quantitative influence of the different additives on the kinetic rate constant, reaction rate data for each additive were fitted to the empirical equation:

$$r = k' w_{\text{ad}}^m \quad (2)$$

where k' is an empirical rate constant for the additive and the relative humidity, w_{ad} is the weight ratio of additive and m the empirical reaction order.

Table 3

Kinetic rate constants and reaction orders in presence of inorganic additives at 71.5°C and 36.7% relative humidity

| Additive | k' (mol/h mol OH ⁻) | m |
|-------------------|-----------------------------------|-------|
| CaCl ₂ | 0.732 | 0.60 |
| NaOH | 0.381 | 0.52 |
| NaCl | 0.063 | -0.12 |

Table 4

The temperature dependent kinetic rate constant values at 71.5°C for calcium hydroxide and calcium hydroxide–additive mixtures

| Sorbent | $k, k_{\text{ad}} \times 10^3$ (mol/h mol OH ⁻) |
|---|---|
| Ca(OH) ₂ | 1.03 |
| Ca(OH) ₂ + CaCl ₂ | 9.7 |
| Ca(OH) ₂ + NaOH | 5.1 |
| Ca(OH) ₂ + NaCl | 0.83 |

The k' and m values obtained for the different additives can be found in Table 3. These results corroborate that calcium chloride removed sulfur dioxide more effectively than sodium hydroxide. On the other hand, sodium chloride appeared to be an inhibitor. By considering that:

$$k' = k_{\text{ad}}(\text{HR})^{1.2} \quad (3)$$

where k_{ad} is the temperature dependent kinetic constant for the additive presence, the k_{ad} values have been determined at 71.5°C and 36.7% of relative humidity and they have been compared with the temperature dependent kinetic constant obtained at the same temperature without the presence of additive. The results are given in Table 4, and it can be seen that at 71.5°C, the kinetic rate constant for calcium hydroxide–calcium chloride mixture is about nine times the rate constant of calcium hydroxide without additives. For sodium hydroxide, the rate constant is about five times higher while for sodium chloride the rate constant is 1.24 times smaller than for calcium hydroxide alone.

4. Conclusions

In this research, the quantitative influence of sulfur dioxide concentration, temperature, relative humidity and the type and amount of the three inorganic additives on the reaction rate between calcium hydroxide and sulfur dioxide have been determined.

The SO₂ concentration (0–3000 ppm) was shown to have no significant influence on the reaction rate at a relative humidity of 38% and at 71.5°C. These results agree with those of Ruiz-Alsop and Rochelle [14] who indicated that sulfur dioxide concentration does not influence the reaction rate at temperatures ranging from 30°C to 90°C; 17–90% relative humidity and sulfur dioxide concentration varying from 0 to 4000 ppm. Since our experiments are within the range of these experimental conditions, we assume that sulfur dioxide concentration will not influence the reaction rate at our other experimental conditions also.

An empirical rate equation, which allows us to quantify the influence of temperature and relative humidity on reaction rate has been developed and an apparent activation energy of 32 kJ/mol Ca(OH)₂ has been calculated. This value, relatively high, demonstrates the weak influence of temperature, but the reaction order of 1.2 with respect to the relative humidity shows its strong influence on reaction rate.

Three inorganic additives were tested to evaluate their quantitative influence on reaction rate. An empirical equation for each additive at 71.5°C and a relative humidity of 36.7% was developed:

$$r = k_{\text{ad}}(\text{HR})^{1.2} w_{\text{ad}}^m \quad (4)$$

The kinetic rate constants for calcium chloride, sodium hydroxide and sodium chloride were found to be respectively, 9, 5 and 0.81 times the rate constant for calcium hydroxide without any additive. The reaction orders for the weight ratio of the same additives were 0.6, 0.52 and -0.12 , respectively. Calcium chloride is the best additive whereas sodium chloride is an inhibitor.

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