Kinetics of the Sulfation of NaCl at Combustion Conditions

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SO_2 and NaCl react in the presence of O_2 and water vapor to produce Na_2SO_4 and HCl. The sulfation of solid NaCl was studied in a fixed-bed reactor in the temperature range 400−600 °C where NaCl, Na_2SO_4, and their mixtures are solid. Other experimental conditions were as follows: 0.3−1.1% SO_2, 3−11% O_2, 0.5−20% H_2O, 2 g of NaCl particles with surface areas of 0.13−0.29 m^2/g, and a total gas flow rate of 15 cm^3/s (at 20 °C). Under the experimental conditions employed, intraparticle diffusion and external mass transfer did not influence the overall rate, and true kinetic data were obtained. The sulfation rate of the solid NaCl was very slow, with only 0.5−1.1% of the NaCl converted to Na_2SO_4 in 3 h. The rate was not strongly temperature dependent, and the activation energy was 17 kJ/mol. The reaction rate depended on SO_2 partial pressure but not on water vapor and O_2 partial pressures. The observed reaction rate was consistent with a mechanism in which Langmuir-type adsorption of SO_2 on the NaCl surface is the rate-limiting step.

Introduction

Either solid or liquid NaCl can react with water vapor and oxygen to produce Na_2SO_4 and HCl.

$$\mathrm{NaCl(s,l)} + {}^1/_2\mathrm{SO_2} + {}^1/_4\mathrm{O_2} + {}^1/_2\mathrm{H_2O} \rightarrow \mathrm{HCl} + {}^1/_2\mathrm{Na_2SO_4(s,l)} \quad (1)$$

In kraft pulp mills, the sulfation of NaCl is of significance in the recovery boilers in which spent pulping liquor—black liquor—is burned. Black liquor typically contains 17−22% sodium, 3−7% sulfur, and 0.5−5% chloride. Sodium and sulfur are present because their compounds constitute the active pulping chemicals, whereas chloride is an impurity whose sources are wood, makeup chemicals, and mill water. Part of the sulfur is released as SO_2 during black liquor combustion and part of the sodium as NaCl. Thus, both are present in the flue gases, and the SO_2 released may be captured by NaCl. This prevents SO_2 emissions and reduces sulfur losses from the system and, at the same time, provides for the purging of chlorides from the cycle, preventing the buildup of chlorides in the system. The HCl emissions produced are, however, harmful and, in addition to detrimental effects on the environment, can cause corrosion in the boiler. The sulfation of NaCl is also used in the Hargreaves process for the production of HCl at temperatures between 430 and 540 °C (*1*). In gas turbine engines, the reaction is important in controlling hot corrosion degradation (*2*). The corrosion results from the deposition of Na_2SO_4 generated by the sulfation of NaCl.

The sulfation of NaCl has been studied by Henriksson and Warnqvist (*3*) and Fielder et al. (*2*). The experimental procedure of Henriksson and Warnqvist (*3*) involved placing Al_2O_3 boats which contained NaCl into a long Al_2O_3 tube within an electrically heated tube furnace. The temperature range studied was from 500 to 800 °C, which includes both solid and molten regions of NaCl and Na_2SO_4 mixtures. The reaction rate exhibited an unexpected flow dependence; i.e., the rate first increased and then decreased with increasing gas flow rate. This may have been a result of mass-transfer effects in the experimental apparatus. An unusual temperature dependence was also observed in this study: the rate of reaction decreased with increasing temperature below 500 °C. The chemical reaction was reported to be the rate-limiting step of this reaction, although this was not consistent with the observed effect of flow rate on the reaction rate. Henriksson and Warnqvist reported that the reaction was of 0.5 order with respect to SO_2 partial pressure and also of 0.5 order with respect to O_2 partial pressure but that the reaction rate was independent of water vapor partial pressure. The following reaction mechanism was suggested: SO_2 and O_2 are adsorbed on the NaCl surface, and the adsorbed species react to form SO_3(ads). The SO_3(ads) reacts with adsorbed water and NaCl to form HCl and Na_2SO_4. The intermediates were postulated to be H_2SO_4(ads) and $NaHSO_4$(ads).

Fielder et al. (*2*) investigated the sulfation of NaCl with mixtures of SO_2 and SO_3 and mainly without any appreciable amounts of water present (less than 20−40 ppm water). A Pt catalyst was used to produce the desired concentration of SO_3 in the mixture. An electrobalance in which a sample of NaCl was suspended was used to follow the reaction. High-pressure mass spectrometric sampling techniques were used to analyze the gas species. The temperature range studied was from 100 to above 650 °C. Under the anhydrous conditions, different products were formed on the NaCl surface at different ranges of temperature, and Cl_2 was detected in the gas phase. Experiments in the presence of water vapor were made only between 400 and 450 °C. The products were Na_2SO_4 and HCl. The overall rate of reaction was reported to be controlled by the chemical reaction step. The rate was found to be first order with respect to SO_3 and also first order with respect to water vapor. No kinetic parameters were given.

In the study of Henriksson and Warnqvist (*3*), the rates depended on the gas flow rate and an unexpected temperature dependence was observed below 500 °C. It was concluded that more reliable kinetic data were needed for this reaction.

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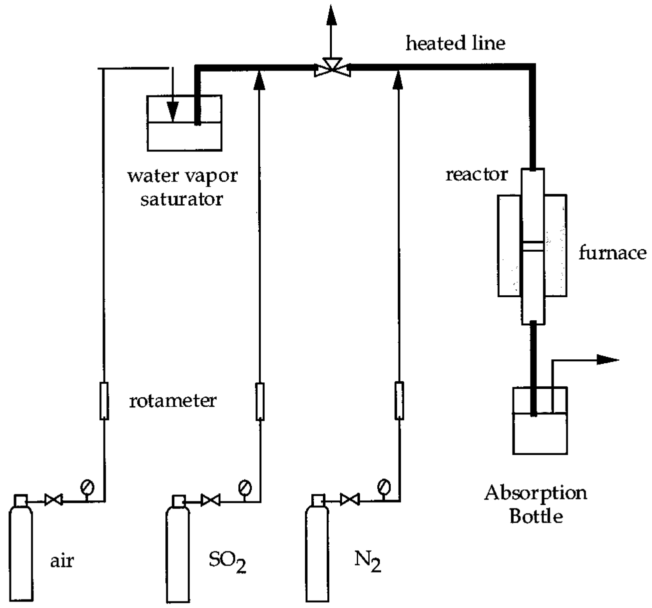

Figure 1. Experimental apparatus.

This study was undertaken to determine the kinetics of sulfation of NaCl by SO_2 in the presence of oxygen and water vapor at temperatures below the melting point.

Experimental Section

The NaCl used in these experiments was prepared by grinding a batch of reagent-grade NaCl (minimum 97% NaCl), sieving, and collecting fractions in the size ranges of 63−90, 90−125, and 125−250 μm. The total surface areas of the NaCl particles, obtained by BET analysis with N_2, were 0.289, 0.181, and 0.134 m^2/g, respectively.

A flow diagram of the experimental system is shown in Figure 1. A fixed-bed reactor consisting of a vertical quartz tube (2-cm i.d.) inside a tube furnace was used in the study. The reactor was constructed of quartz glass to avoid catalytic oxidation of SO_2 to SO_3 at high temperatures on metallic surfaces. The NaCl was placed on a porous quartz glass support in the center of the reactor. The operating temperature was measured by a thermocouple inserted into the NaCl bed.

The kinetic studies were conducted by passing a mixture of SO_2, O_2, water vapor, and N_2 over preheated NaCl samples. Cylinders containing 5% SO_2 in N_2, air, and nitrogen were used to prepare the gas mixtures. The water vapor concentration was controlled by saturating the air stream with water vapor at a constant temperature prior to mixing it with SO_2 and N_2.

The rate of reaction was monitored by absorbing the HCl generated in deionized water and measuring the chloride ion concentration with a specific ion electrode. The product gas lines from the reactor were heated to prevent HCl and water vapor from condensing in them. A typical experiment was run for 3 h, and the absorbed HCl was measured every 30 min.

A preliminary test was made to determine whether all of the HCl generated in the reactor would be absorbed in a single absorption bottle. A gas containing 1% HCl in N_2 was passed through two adsorption bottles in series. At flow rates equal to or less than 15 cm^3/s (at 20 °C), more than 98% of the chloride input was collected in the first bottle. Thus, it was decided that one absorption bottle was sufficient for the HCl measurement if the gas flow rate did not exceed 15 cm^3/s.

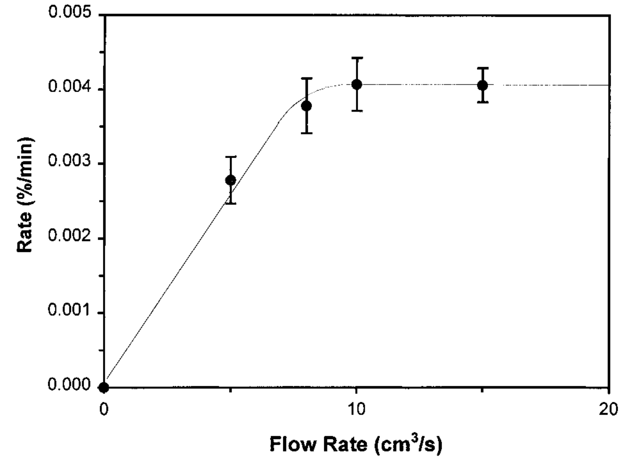

Figure 2. NaCl conversion rates at total flow rates of 5, 8, 10, and 15 cm^3/s (20 °C, 1 atm) at 500 °C, 0.3% SO_2, 5% O_2, 10% H_2O, and 2 g of 125−250-μm NaCl.

Table 1. Comparison of the Degree of Conversion Obtained by the Residual Solid Analysis and the Gas Analysis (Results Expressed as Conversion of NaCl)

run	residual solid anal., %	gas anal., %
10	0.64	0.61
14	0.83	0.81
20	0.41	0.43

The residual solid products from several runs were sent to the Weyerhaeuser Company analytical laboratory in Tacoma, WA, for sodium, chloride, and sulfate analysis. The conversion of NaCl was calculated from both the residual solid composition and the product gas analysis. The comparison is shown in Table 1. The conversions calculated from both methods agree very well.

Results and Discussion

Preliminary Experiments: Effects of Gas Flow Rate and Particle Size. The initial experiments were run to determine the operating conditions at which external mass transfer through the gas boundary and diffusion inside the particles would not affect the reaction rate. For the external mass-transfer tests, the initial reaction rates were measured at different gas flow rates at 500 °C as shown in Figure 2. The reaction rate increased with an increase in flow rate below 10 cm^3/s (20 °C, 1 atm) and was constant above this gas flow rate. This result implies that external mass transfer through the gas boundary is negligible at total gas flow rates above 10 cm^3/s. Experiments made at 600 °C showed that the external mass-transfer effects at that temperature were negligible at total flow rates of 15 cm^3/s (20 °C, 1 atm) and above (*4*). Since 600 °C was the highest temperature studied, the experimental data were obtained at a total flow rate of 15 cm^3/s (20 °C, 1 atm) at all conditions.

Particles of different sizes, 125−250, 90−125, and 63−90 μm, were used to evaluate whether intraparticle diffusion was important. The conversion vs time data for the different particle sizes at the highest temperature studied, 600 °C, are shown in Figure 3. Higher rates on a mass basis were obtained for smaller particles. However, the surface areas of the particles in the different size ranges were different, and a reaction

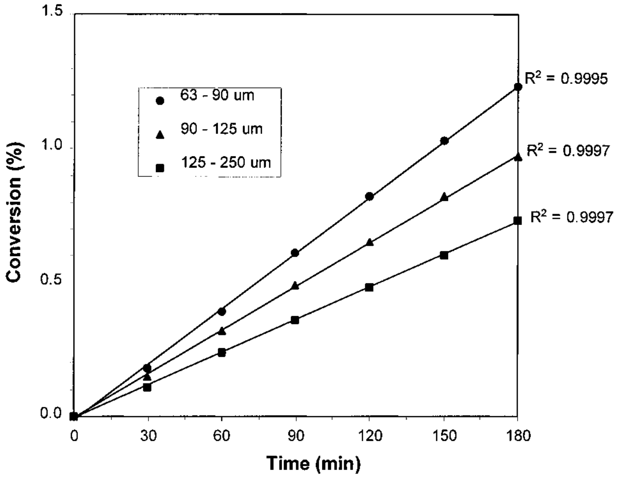

Figure 3. Conversion vs time data for 125–250-, 90–125-, and 63–90-μm particles at 15 cm^3/s (20 °C, 1 atm) total flow rate, 500 °C, 0.3% SO_2, 5% O_2, 10% H_2O, and 2 g of NaCl.

Table 2. Comparison of the Total Surface Areas and Rate Constants of Different Particle Sizes at a Total Gas Flow Rate of 15 cm^3/s (20 °C, 1 atm), 500 °C, 0.3% SO_2, 5% O_2, 10% H_2O, and 2 g of NaCl

particle size range, μm	total surf area, (m^2/g)	rate const, mol/(m^2·atm·min)
63–90	0.289	1.53×10^{-3}
90–125	0.181	1.21×10^{-3}
125–250	0.134	1.21×10^{-3}

rate constant based on the total surface area (mol/(m^2·atm·min)) was calculated for each size range (*4*). The results in Table 2 show that the rate constants for different particle sizes were almost the same. This implies that intraparticle diffusion had no significant effect on the measured rate.

As can be seen in Figure 3, the conversions of NaCl were low: depending on the particle size, the conversions in 180 min were only 0.7–1.2%. For each particle size, the conversion increased linearly with time in the range studied. For high conversions, a linear increase in the conversion of a solid in a gas–solid reaction usually indicates external mass-transfer limitations. For the low conversions obtained in this study, both kinetics and external mass transfer are linear with time. Based on the effect of gas flow rate, there were no external mass-transfer limitations at the experimental conditions. The linear increase in conversion thus indicates that the reaction surface area did not change during the reaction and that diffusion through a layer of Na_2SO_4 forming on the surface of NaCl did not limit the reaction rate. These conclusions are reasonable for the low conversions.

Based on the preliminary experiments, the reaction rate was limited by chemical kinetics. Experiments were made at different temperatures and SO_2, O_2, and H_2O concentrations to obtain the kinetics of the reaction.

Effect of Temperature. The conversion vs time data for the sulfation of NaCl at different temperatures from 400 to 600 °C are shown in Figure 4. The same linear increase of conversion with time as discussed earlier is seen at each temperature. The rate of SO_2 capture by NaCl was not strongly temperature dependent, increasing by slightly more than a factor of 2 over the temperature range 400–600 °C.

The reaction rate increased with temperature throughout the temperature range studied. An Arrhenius plot of the rate is shown in Figure 5. The activation energy of the reaction was determined to be 17.3 kJ/mol, which is low for a chemical kinetics-controlled process. The low activation energy suggests that a physical process such as adsorption or desorption was the rate-controlling step.

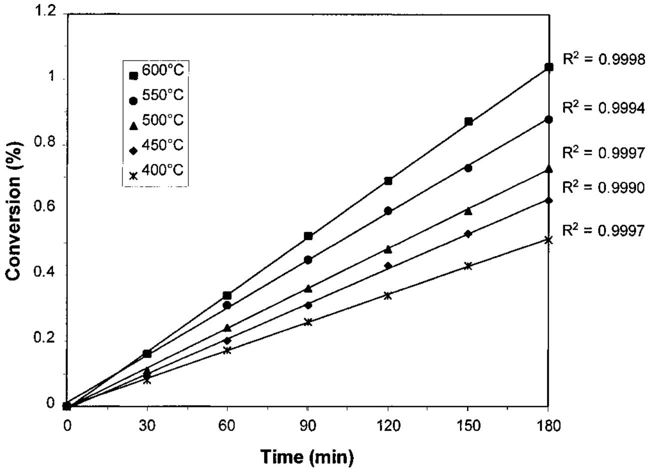

Figure 4. Conversion vs time data at temperatures 400, 450, 500, 550, and 600 °C at 15 cm^3/s (20 °C, 1 atm) total flow rate, 0.3% SO_2, 5% O_2, 10% H_2O, and 2 g of 125–250-μm NaCl.

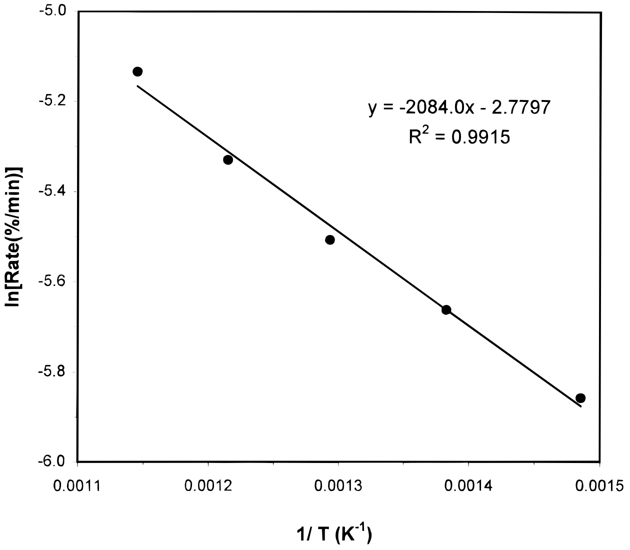

Figure 5. Arrhenius plot for the data at 15 cm^3/s (20 °C, 1 atm) total flow rate, 0.3% SO_2, 5% O_2, 10% H_2O, and 2 g of 125–250-μm NaCl.

The unusual temperature dependence observed in the study of Henriksson and Warnqvist (*3*) was not detected in our experiments. The reason for the temperature dependency in the previous study is not clear. It could have been the result of liquid sodium pyrosulfate formation as suggested by Lloyd-George (*5*) in his investigation of the sulfation of Na_2CO_3. In the presence of the liquid sodium pyrosulfate, the mechanism of sulfation may be different than in the absence of it, and this may lead to unusual temperature behavior. The temperature range in which liquid sodium pyrosulfate is stable depends on the SO_3 concentration. This range was 350–550 °C in the study of Lloyd-George (*5*). The SO_3 in those experiments was formed by oxidation of SO_2, catalyzed by the metallic parts in the experimental apparatus. The SO_3 concentrations were not reported, however. In our study, the high-temperature parts of the equipment were nonmetallic, so little oxidation of SO_2 to SO_3 should have occurred. Thus, there was little possibility of sodium pyrosulfate formation in our study.

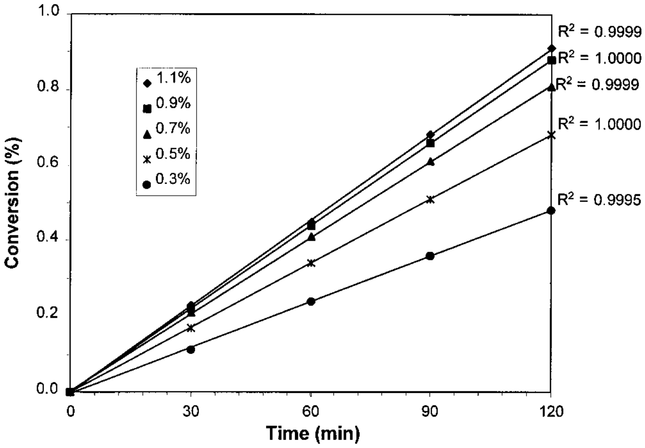

Figure 6. Conversion vs time data at 0.3, 0.5, 0.7, 0.9, and 1.1% SO_2 concentrations at 15 cm^3/s (20 °C, 1 atm) total flow rate, 500 °C, 5% O_2, 10% H_2O, and 2 g of 125−250-μm NaCl.

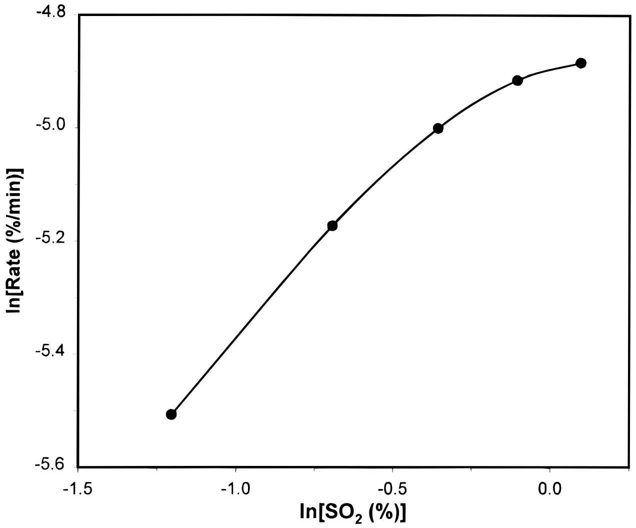

Figure 7. Relationship between ln(rate (%/min)) and ln(SO_2 (%)) at 0.3−1.1% SO_2, 5% O_2, and 10% H_2O.

It is not known whether SO_3 was formed in the study of Henriksson and Warnquist.

Another possibility for the temperature effect observed by Henriksson and Warnquist is that the sulfation rate was affected by a decrease in the internal surface area of the solid material due to sintering. If the decrease of the surface area is larger than the corresponding increase in the rate constant, the observed reaction rate decreases as the temperature is increased. A similar temperature influence on the sulfation of Na_2CO_3 has been shown by Backman et al. (*6*) to have been caused by sintering.

Effect of SO_2 Concentration. The SO_2 concentration range studied was from 0.3 to 1.1%. The conversion vs time data for different SO_2 concentrations are shown in Figure 6. The data show that the rate increases more rapidly with increasing SO_2 partial pressure at lower SO_2 partial pressures than at higher SO_2 partial pressures.

The data in Figure 6 were analyzed further to find the reaction order with respect to SO_2. To find the reaction order, the logarithm of the chemical kinetic rate was plotted against the logarithm of the SO_2 concentration as shown in Figure 7. The chemical kinetic rate increased with increasing SO_2 concentrations and was less dependent on SO_2 concentration at high rather than at low SO_2 concentrations. The slope of this curve, which gives the order of the reaction with respect to SO_2, decreased from 0.67 at the lowest SO_2 concentrations used to 0.16 at the highest. The nonlinear dependence of the rate on SO_2 concentration in Figure 7 indicates that the rate is not of constant order in SO_2 even though SO_2 is involved in the rate-limiting step of the reaction. A more complicated rate expression needs to be used to present the SO_2 dependence of the rate.

Effects of H_2O and O_2 Concentrations. The O_2 and H_2O(v) concentration ranges studied were from 3 to 11% and from 0.5 to 20%, respectively. The conditions of these studies were 15 cm^3/s (20 °C, 1 atm) total gas flow rate, 500 °C, 0.3% SO_2, and 2 g of 125−250-μm NaCl. The reaction rate was independent of O_2 and H_2O concentration at the conditions employed. This indicates that oxygen and water vapor are involved in a fast reaction step which does not control the overall rate of reaction.

Proposed Reaction Mechanism. The following mechanism had been suggested by Henriksson and Warnqvist (*3*) for the sulfation of NaCl by SO_2 in the absence of SO_3:

$$SO_2(g) \leftrightarrow SO_2(ads)$$

$$O_2(g) \leftrightarrow O_2(ads)$$

$$H_2O(g) \leftrightarrow H_2O(ads)$$

$$SO_2(ads) + {}^1/_2O_2(ads) \rightarrow SO_3(ads)$$

$$SO_3(ads) + H_2O(ads) \rightarrow H_2SO_4(ads)$$

$$H_2SO_4(ads) + NaCl(s) \rightarrow HCl(g) + NaHSO_4(ads)$$

$$NaHSO_4(ads) + NaCl(s) \rightarrow Na_2SO_4(s) + HCl(g)$$

In this mechanism, SO_2(g), O_2(g), and H_2O(g) are first adsorbed on the surface of NaCl and then SO_2(ads) reacts with O_2(ads) to form SO_3(ads). H_2O(ads) reacts with SO_3(ads) to form H_2SO_4(ads). The products, Na_2SO_4 and HCl, are obtained from the reaction between H_2SO_4(ads) and NaCl via a $NaHSO_4$(ads) intermediate.

Based on the results of our experiments, the apparent activation energy of the overall reaction is quite low, which is consistent with a physical adsorption−desorption process as being the rate-controlling step. Based on the effects of the gas concentrations, SO_2 is involved in the rate-limiting step, whereas O_2 and H_2O are not. Combining this information with the proposed mechanism suggests that the adsorption of SO_2(g) on the surface of NaCl is the rate-limiting step. Additional support for this conclusion is that the chemical kinetic rate increased as SO_2 concentration increased and that the reaction order with respect to SO_2 decreased as SO_2 concentration increased. This is typical for Langmuir-type adsorption (*7*).

Reaction Rate Analysis. The overall reaction rate was limited by chemical kinetics at the conditions investigated in this study. The results implied that the adsorption of SO_2 on the surface limited the overall reaction rate. Thus, the overall rate of reaction can be approximated by the rate of adsorption of SO_2. Langmuir isotherms are used to describe the adsorption process. The model is based on the assumption that the surface is energetically ideal and that forces of interaction between adsorbed species are negligible. The adsorption rate is assumed to be proportional to the partial pressure of the adsorbed species and the fraction of the solid surface unoccupied. The resulting rate equation is

$$-r_{SO_2} = S' \frac{kP_{SO_2}}{1 + K_1P_{SO_2} + K_2P_{O_2} + K_3P_{H_2O}} \tag{2}$$

where $-r_{SO_2}$ = rate of disappearance of SO_2, mol/(min·g); k = reaction rate constant, mol/(m^2·min·atm); p_i = partial pressure of gas i, atm; S' = internal surface area, m^2/g; K_1 = adsorption equilibrium constant of SO_2, atm^{-1}; K_2 = adsorption equilibrium constant of O_2, atm^{-1}; and K_3 = adsorption equilibrium constant of H_2O, atm^{-1}. If $K_2p_{O_2}$ and $K_3p_{H_2O}$ are much smaller than 1 and $K_1P_{SO_2}$, the reaction rate can be expressed as

$$-r_{SO_2} = S' \frac{kp_{SO_2}}{1 + K_1p_{SO_2}} \tag{3}$$

The same rate expression can be obtained by assuming that only SO_2 adsorbs on the surface, and that the adsorbed SO_2 reacts with gas phase O_2 and H_2O to form H_2SO_4(ads).

From the overall reaction stoichiometry

$$2(-r_{SO_2}) = -r_{NaCl} \tag{4}$$

and the rate of disappearance of NaCl, $-r_{NaCl}$ can be presented as

$$-r_{NaCl} = \frac{1}{M_{NaCl}} \frac{dX}{dt} \tag{5}$$

where M_{NaCl} = molecular weight of NaCl, 58.4 g/mol, and X = conversion of NaCl. Thus,

$$S' \frac{kp_{SO_2}}{1 + K_1p_{SO_2}} = \frac{1}{2M_{NaCl}} \frac{dX}{dt} \tag{6}$$

Rearranging gives

$$\frac{2S'M_{NaCl}}{dX/dt} = (K_1/k) + (1/k)\frac{1}{P_{SO_2}} \tag{7}$$

Thus, the reciprocal of dX/dt should be a linear relationship of the reciprocal of SO_2 partial pressure. In Figure 8, a plot of $2M_{NaCl}$/(dX/dt) vs $1/P_{SO_2}$ is shown. The relationship is linear, which indicates good agreement between the model and the data.

The intercept and slope were obtained by linear regression analysis, and the values of K_1 and k at 500 °C were calculated from them. They were $k = 172 \pm 12$ atm^{-1} and $K_1 = 1.32 \times 10^{-3} \pm 0.11 \times 10^{-3}$ (mol/(m^2·atm·min). Thus, the kinetic rate of this reaction at 500 °C can be presented as

$$-r_{NaCl} = r_{HCl} = 2(-r_{SO_2}) = S' \frac{2.64 \times 10^{-3} p_{SO_2}}{1 + 172p_{SO_2}} \tag{8}$$

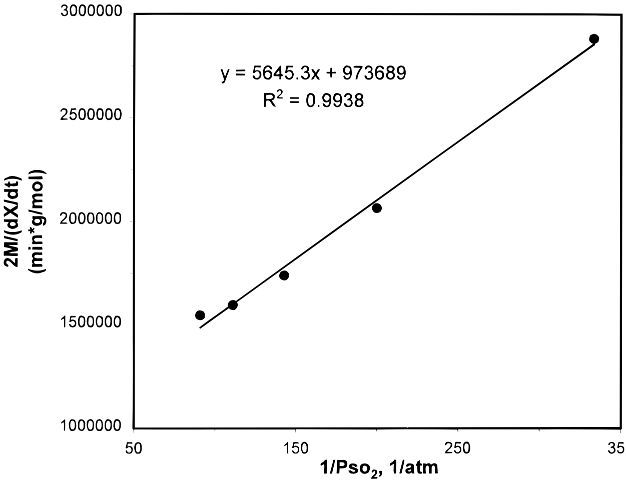

Figure 8. Relationship between 2M/(dX/dt) and $1/p_{SO_2}$.

Conclusions

The sulfation of NaCl in the solid state is a relatively slow reaction. The rate of reaction depends on the partial pressure of SO_2 but not on the partial pressures of O_2 and H_2O for the range of conditions of 0.3−1.1% SO_2, 3−11% O_2, 0.5−20% H_2O, and 400−600 °C. The observed reaction rate is consistent with a mechanism in which the adsorption of SO_2 on the NaCl surface is the rate-limiting step. The kinetic parameters for a Langmuir-type adsorption were determined at 500 °C as well as the overall activation energy for the temperature range 400−600 °C. The importance of the sulfation of solid NaCl as well solid Na_2CO_3 in recovery boilers is discussed in a separate publication (*8*).

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