SO₂ Removal by NH₃ Gas Injection: Effects of Temperature and Moisture Content

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The removal of SO₂ by NH₃ gas injection at various temperatures and moisture contents has been studied experimentally. The product compositions of the NH₃-SO₂-H₂O vapor reactions were also reported. A thermodynamic analysis was carried out to predict the SO₂ removal as well as the product compositions. Both the experimental results and thermodynamic analysis indicated that SO₂ removal and the product compositions are sensitive to the reaction temperature. Moisture content, once in large excess of the stoichiometric requirement, does not have a strong effect on the product compositions but plays an important role in the SO₂ removal.

Introduction

Sulfur dioxide removal from flue gases is a goal of many air pollution engineers. Significant efforts in the development of new flue gas desulfurization (FGD) technologies are being made. Major processes related to FGD technologies include water scrubbing, metal ion solutions, catalytic oxidation, dry or semidry adsorption, wet lime or limestone scrubbing, double alkali process, and ammonia scrubbing.

Sulfur dioxide removal from coal-fired power plants by NH₃ gas injection is a dry FGD technique that has been studied by several researchers. Shale (1971, 1973) performed both bench-scale and pilot plant tests and showed that a complete removal of SO₂ was feasible when NH₃ was injected at a molar ratio of NH₃ to SO₂ of slightly less than 2. In his study, NH₃ was injected into the gas stream with water vapor which saturated and cooled the gas stream to below the sublimation temperature (60 °C) of anhydrous ammonium sulfite ((NH₄)₂SO₃). Tock et al. (1979) presented a thermodynamic analysis of the SO₂-NH₃-H₂O vapor system based on the equilibrium data provided by St. Clair (1937) and Scargill (1971). They assumed the reaction products to be either (NH₄)₂SO₃ or (NH₄)₂-SO₃·H₂O. Stromberger (1984) conducted a bench-scale study of the SO₂ removal by NH₃ gas injection in simulated flue gases. The results were similar to the equilibrium calculations of Tock et al. (1979), and indicated that SO₂ removal dropped to near zero at a temperature of around 54 °C. On the other hand, a pilot-scale study performed by Keener and Davis (1988) showed that a high SO₂ removal from flue gas by NH₃ injection was possible at temperatures above 54 °C. They reported that the SO₂ removal was in excess of 95% at about 2:1 molar injection ratios of NH₃/SO₂ for temperatures below 85 °C.

The reaction products of the SO₂-NH₃-H₂O vapor system are solid particles. Shale (1973) and Keener and Davis (1988) postulated the reaction products to be (NH₄)₂-SO₃ and ammonium bisulfite (NH₄HSO₃). Hartley and Matteson (1975) conducted room temperature experiments of NH₃ and SO₂ reactions under humid conditions, and found by X-ray diffraction that ammonium sulfate ((NH₄)₂SO₄) was the product under excess moisture
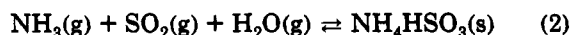
conditions. Stromberger (1984) used X-ray diffraction and identified the product particles to be (NH₄)₂SO₄ crystals.

Although a number of studies on the removal of SO₂ from flue gases by NH₃ injection have been conducted, there is disagreement on the operating condition (such as temperature) that a high removal efficiency can be obtained. This may due to different moisture contents incorporated in the previous studies. For example, Stromberger's experiment (1984) was conducted at a moisture content of about 2% by volume, while the study of Keener and Davis (1988) was performed under a much higher moisture content (5-11%) which is typical in a boiler system. There is also controversy in the literature as to what products are formed. An understanding of the compositions of the product particles is important since it indicates the NH₃ injection rate required to remove the SO₂ pollutant. An excessive amount of NH₃ gas may result in a secondary pollution problem.

A study of the NH₃-SO₂ reactions at trace water conditions was performed by Bai et al. (1992). The compositions of the product as well as the particle size distributions were presented as functions of residence time and inlet gas concentrations. In the present paper, NH₃-SO₂-H₂O vapor reactions at various temperatures and moisture contents are studied. The SO₂ removal, NH₃ utilization, and product compositions are reported. The experimental results are compared to the predictions of a thermodynamic equilibrium calculation considering several possible reaction schemes.

Equilibrium Chemistry

When gaseous NH₃, SO₂, and water vapor are mixed, white crystallite materials are formed. Shale (1973) postulated the following chemical reactions:

$$2NH_3(g) + SO_2(g) + H_2O(g) \rightleftharpoons (NH_4)_2SO_3(s) \quad (1)$$

$$NH_3(g) + SO_2(g) + H_2O(g) \rightleftharpoons NH_4HSO_3(s) \quad (2)$$

St. Clair (1937) conducted an equilibrium study and indicated that ammonium pyrosulfite ((NH₄)₂S₂O₅) and (NH₄)₂SO₃·H₂O could also be the products,

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Table 1. Possible NH_3-SO_2-H_2O Vapor Reactions and Their Equilibrium Constants

possible reactions	equilib expressions	temp range °C	sources[a]
$(NH_4)_2S_2O_5(s) = 2NH_3 + 2SO_2 + H_2O$	$K_p = \exp(94.6 - 39144/T)$	60–110	1
	$K_p = \exp(96.5 - 40767/T)$	0–23	2
$(NH_4)_2SO_3(s) = 2NH_3 + SO_2 + H_2O$	$K_p = \exp(73.8 - 30601/T)$	60–110	1, 3
	$K_p = \exp(76.6 - 32630/T)$	0–23	2
$(NH_4)_2SO_3H_2O(s) = 2NH_3 + SO_2 + 2H_2O$	$K_p = \exp(93.8 - 38062/T)$	60–110	1, 3
	$K_p = \exp(96.7 - 40090/T)$	0–23	2, 3
$NH_4HSO_3(s) = NH_3 + SO_2 + H_2O$	$K_p = \exp(53.8 - 22116/T)$	60–110	1, 3
	$K_p = \exp(54.7 - 22928/T)$	0–23	2, 3

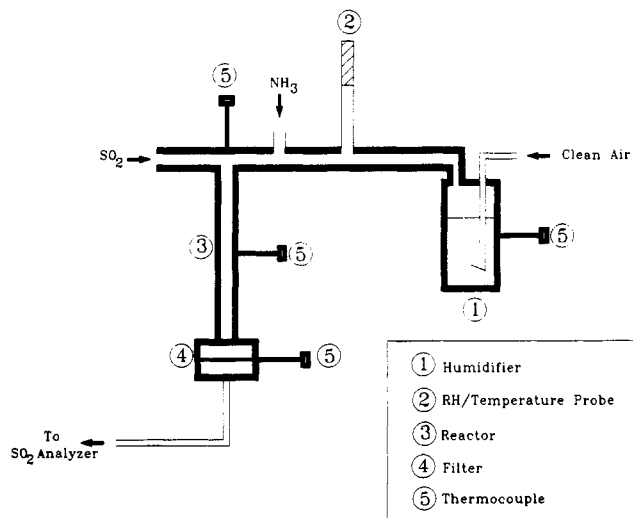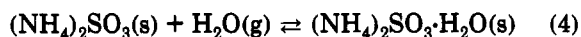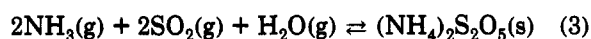[a] 1, St. Clair (1937); 2, Scargill (1971); 3, Tock et al. (1979).

Figure 1. Schematic diagram of the NH_3-SO_2-H_2O reactor system.

$$2NH_3(g) + 2SO_2(g) + H_2O(g) \rightleftharpoons (NH_4)_2S_2O_5(s) \quad (3)$$

$$(NH_4)_2SO_3(s) + H_2O(g) \rightleftharpoons (NH_4)_2SO_3 \cdot H_2O(s) \quad (4)$$

The equilibrium relationship of any of the above reactions of the form $aA(g) + bB(g) + cC(g) + dD(s) = E(s)$, is given by

$$K_p = (P_{A,in} - aX)^a(P_{B,in} - bX)^b(P_{C,in} - cX)^c \quad (5)$$

where K_p is the equilibrium constant of the reaction, X is the mole fraction of solid E formed from the gas-phase reaction in a state of equilibrium; $P_{i,in}$ (i = A, B, or C) is the inlet partial pressure of the gaseous reactant A, B, or C. Therefore, if the inlet concentration of each gas is known, eq 5 can be solved to obtain the SO_2, NH_3, and H_2O vapor concentrations at equilibrium. The equilibrium constants for reactions 1–4 are summarized in Table 1.

There was also a possibility that an ideal mixture of the above solid products is formed during the reaction. Equilibrium calculations of an ideal mixture of the possible products were obtained by Bai et al. (1992) and Scott and Lamb (1970).

Experimental System

Figure 1 shows the schematic diagram of the reactor system used to study the NH_3-SO_2 reaction under humid conditions. Gas inlet concentrations were controlled using mass flow controllers (MKS, Andover, MA). Compressed air was passed through a filtration device (Balston, Haverhill, MA) to remove CO_2 and hydrocarbons and then dried and cleaned by being passed through a silica gel air dryer and a 0.2-μm Gelman air filter (AcroFlow II). The clean air was then saturated with water vapor in a temperature-controlled humidifier to obtain the desired water vapor content. The system was designed to ensure

that no water droplets were carried by the air stream. The relative humidity (RH) was then measured by a Vaisala HMI31/HMP36 relative humidity/temperature sensor system, with accuracies of ±2% RH and ±0.3 °C for humidity and temperature, respectively. The NH_3 gas (4.5% NH_3 in N_2; Linde Specialty Gas) was introduced into the air stream and then mixed with SO_2 gas (1.02% SO_2 in N_2) in a union tee junction. Immediately after mixing, the gases entered a laminar flow tube reactor that was made of stainless steel with inside diameter of 6.4 mm. Temperatures of the entire reaction system were controlled within ±1 °C using temperature controllers and heating tapes. Particles formed from gas-phase reactions were collected on a 47-mm glass fiber filter (Pallflex, Putnam, CT) where the temperature was maintained the same as the reactor temperature. The relative humidity and the temperature of the inner reactor tube were recorded and controlled in a stable condition for each experiment. The effect of reactor residence time on the sulfur dioxide removal is minimum at residence times longer than 0.4 s (Bai et al., 1991; Bai, 1992). Therefore the data to be presented are those done at a residence time of 0.9 s. Several temperature and moisture conditions were chosen at random and repeated two additional times to check for reproducibility.

The total sulfur removal (in terms of SO_4^{2-}), the total sulfite (in terms of SO_3^{2-}), and the ammonia utilization (in terms of NH_4^+) were determined by wet chemical analysis of the collected particles. The collected particles were extracted by washing the filter and the reactor walls with double-distilled water. The SO_3^{2-} concentration in the extracted solution was determined by iodide–iodate titration (Standard Methods, 1985). The SO_3^{2-} measurement was completed within 10 min after each reaction experiment to minimize its oxidation by ambient air. The SO_4^{2-} concentration was determined by oxidizing all sulfur compounds and then measured gravimetrically by precipitating as $BaSO_4$ (Standard Methods, 1985). The NH_4^+ concentration was determined by titration with a hypochlorite solution followed by a back-titration with a standard sodium thiosulfate solution (Kolthoff and Sandell, 1952). All wet chemical analysis techniques performed in this study were calibrated using standard solutions.

Results and Discussion

Room Temperature Experiments. Figure 2 shows the SO_2 removal efficiency at various moisture contents (0–57% RH) for an inlet SO_2 concentration of 3000 ppm and three different NH_3 inlet concentrations of 3000, 6000, and 9000 ppm. The temperature was kept constant at 23.5 ± 1 °C. As can be seen, the moisture content has a pronounced effect on the SO_2 removal efficiency in the test range of 0–10% RH (corresponds to 0–3000 ppm moisture content at 23.5 °C). No further increase in the SO_2 removal efficiency is observed beyond the moisture content of 6000 ppm.
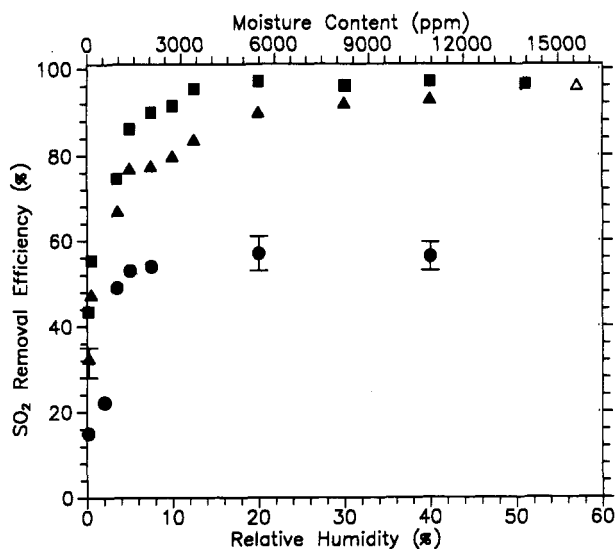
Figure 2. Effect of relative humidity on SO_2 removal at a temperature of 23.5 ± 1 °C and an inlet SO_2 concentration of 3000 ppm: (■) NH_3 inlet concentration of 9000 ppm; (▲) NH_3 inlet concentration of 6000 ppm; (●) NH_3 inlet concentration of 3000 ppm.

For moisture contents below 3000 ppm, water vapor is the limiting factor in the determination of SO_2 removal efficiency. These were also reported by equilibrium calculations performed by Bai et al. (1992). The products formed at low moisture contents are expected to be different from those formed at high moisture contents. The products at near anhydrous conditions were discussed by Bai et al. (1992), and were conjectured to be NH_3SO_2, $(NH_3)_2SO_2$, and $(NH_4)_2S_2O_5$. On the other hand, the products at humid conditions are mostly the 2:1 sulfites, $(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$, as determined by wet chemical analysis in this study.

The SO_2 removal efficiencies for inlet NH_3 concentrations of 6000 and 9000 ppm at higher moisture contents approach 100%. However, the maximum removal efficiency for an inlet NH_3 concentration of 3000 ppm is only around 57% even in tests conducted at a high moisture content. This is due to the formation of 2:1 NH_3/SO_2 reaction products in addition to the 1:1 products. The total NH_3/SO_2 reaction ratio was about 1.3 as determined by wet chemical analysis. Therefore, it may not form a pure 1:1 reaction product even when the molar injection ratio of NH_3/SO_2 is 1.

The reaction products for inlet NH_3 and SO_2 concentrations of 6000 and 3000 ppm, respectively, and a moisture content of 20% RH were also analyzed by X-ray diffraction. The diffraction pattern is shown in Figure 3. As compared to standard patterns (Hanawalt Method Search Manual, 1977), the only identifiable product was $(NH_4)_2SO_4$ (peaks at 2θ = 20.5, 29.2, and 16.6). However, according to Stromberger (1984), the diffraction pattern of $(NH_4)_2SO_3 \cdot H_2O$ is similar to that of $(NH_4)_2SO_4$. Therefore it is also possible that $(NH_4)_2SO_3 \cdot H_2O$ is one of the products of the $NH_3-SO_2-H_2O$ vapor reactions. There are also other undefined peaks which have intensities stronger than 10%. It seems that X-ray diffraction is not an appropriate method to identify the products of $NH_3-SO_2-H_2O$ vapor reactions until more identification files are available.

High-Temperature Experiments. Although commonly used in many pilot-scale studies, an SO_2 analyzer is judged to be inappropriate for measuring the outlet SO_2 concentration by NH_3 injection at temperatures higher than the ambient condition. This is because the $NH_3-SO_2-H_2O$ vapor reactions are very sensitive to the reaction

temperature. The SO_2 removal increases as the temperature decreases. It is very difficult to concisely control the temperature of the gas analyzer. Therefore measurements made by an SO_2 gas analyzer may lead to an artifact increase of the SO_2 removal efficiency at high temperatures.

On the other hand, the wet chemical analysis is useful in providing information on the amount of total sulfur removal, as well as the concentration ratios of SO_3^{2-}/SO_4^{2-} and NH_4^+/SO_4^{2-} in the reaction products. However, it is not possible to distinguish between the 1:1 products of $(NH_4)_2S_2O_5$ and NH_4HSO_3 in the present study. This is because on dissolving into water, $(NH_4)_2S_2O_5$ forms the NH_4HSO_3 (Marks and Ambrose, 1937),

$$(NH_4)_2S_2O_5(s) + H_2O(l) = 2NH_4HSO_3(aq) \qquad (6)$$
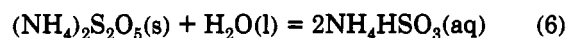
The 2:1 products, $(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$, are also not distinguished. However, since the focus of this study is on the total sulfur removal and the ammonia utilization, distinction of these products is not of major concern.

Figure 4 shows the NH_4^+/SO_4^{2-} and SO_3^{2-}/SO_4^{2-} ratios as a function of the reactor temperature at a water vapor content of 2.7% by volume. The symbols are experimental data with standard deviations of repeated experiments. The curves are regression results of the experimental data. It is seen from the plot of the NH_4^+/SO_4^{2-} ratio that a mixture of 1:1 and 2:1 products tends to form at lower temperatures. The 2:1 products become dominant as temperature increases. This indicates that less NH_3 gas may be required at lower temperatures for removing SO_2 gas.

It is also seen in Figure 4 that the ratio of SO_3^{2-} versus SO_4^{2-} (total sulfur) does not show a very clear trend. The average SO_3^{2-}/SO_4^{2-} ratio of all experimental tests is 0.74. This means that sulfite particles are the dominant products of reaction. The oxidation of sulfites to sulfates is believed to occur after product particles are collected on the filter, or after dissolution in the distilled water. According to St. Clair (1937), $(NH_4)_2SO_3$ and NH_4HSO_3 are easily oxidized to form $(NH_4)_2SO_4$ in comparison to $(NH_4)_2S_2O_5$. Therefore the following reaction schemes may occur on the filter or in the product solution,

$$(NH_4)_2SO_3(s,aq) + {}^1/_2O_2(g) \rightleftarrows (NH_4)_2SO_4(s,aq) \qquad (7)$$

$$NH_4HSO_3(s,aq) + {}^1/_2O_2(g) + NH_3(g) \rightleftarrows$$
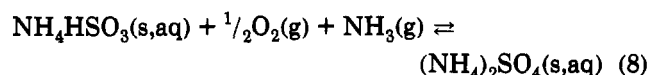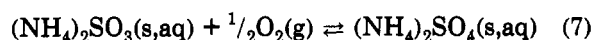$$(NH_4)_2SO_4(s,aq) \qquad (8)$$

Figure 5 illustrates the temperature effect on the total sulfur removal at a water vapor content of 2.7% by volume. The symbols are experimental data, and the lines represent thermodynamic predictions assuming products to be either NH_4HSO_3, $(NH_4)_2SO_3$, or the ideal mixture of the two 2:1 products ($(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$). The theoretical predictions were made using the thermodynamic data of St. Clair (1937) listed in Table 1. It is seen that the theoretical predictions of 1:1 and 2:1 products agree well with the experimental data at lower temperatures. However, assuming NH_4HSO_3 as the product tends to underestimate the total sulfur removal at higher temperatures. $(NH_4)_2SO_3$ or the ideal mixture of the two 2:1 products appear to be the main products at higher temperatures. This observation is confirmed with the experimental results of the NH_4^+/SO_4^{2-} ratio plotted in Figure 4. An attempt has also been made by assuming an ideal mixture of all four possible sulfites (NH_4HSO_3, $(NH_4)_2S_2O_5$, $(NH_4)_2SO_3$, and $(NH_4)_2SO_3 \cdot H_2O$) as the products. The attempt

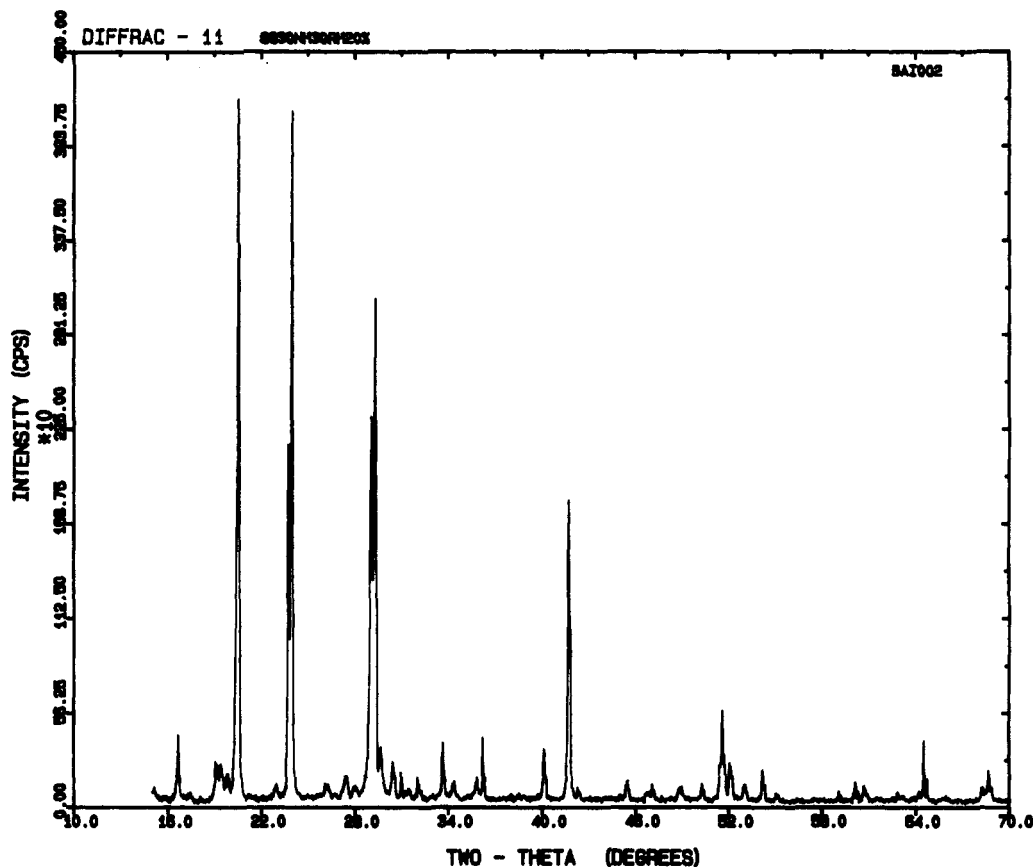**Figure 3.** X-ray diffraction result of NH_3–SO_2 reaction products at a temperature of 23.5 ± 1 °C and relative humidity of 20%. The inlet NH_3 and SO_2 concentrations are 6000 and 3000 ppm, respectively.
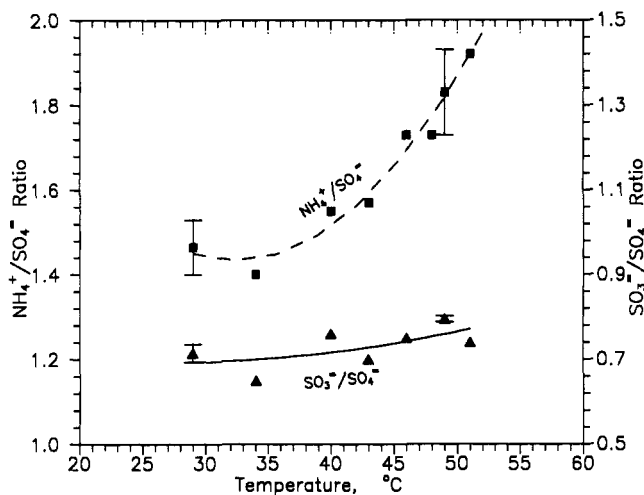

Figure 4. NH_4^+/SO_4^{2-} and SO_3^{2-}/SO_4^{2-} ratios from wet chemical analysis as a function of reaction temperature at H_2O = 2.7% by volume. The inlet NH_3 and SO_2 concentrations are 6000 and 3000 ppm, respectively: (■) represents the (NH_4^+/SO_4^{2-}) ratio; (▲) represents the (SO_3^{2-}/SO_4^{2-}) ratio; lines are their regression curves.

did not yield good agreement with the experimental data. It seems that an ideal mixture of the four vapor products is not possible. Instead, the system may involve the decomposition of one product completely to form another product (that is, an univariant system). One example, as observed by St. Clair (1937), is the decomposition of $(NH_4)_2S_2O_5$ completely to form NH_4HSO_3 at lower temperatures as the moisture content is in excess of stoichiometric requirements. Therefore it may be concluded that the 1:1 product of NH_3/SO_2 reaction is NH_4-HSO_3. However, an ideal mixture of the 2:1 sulfites
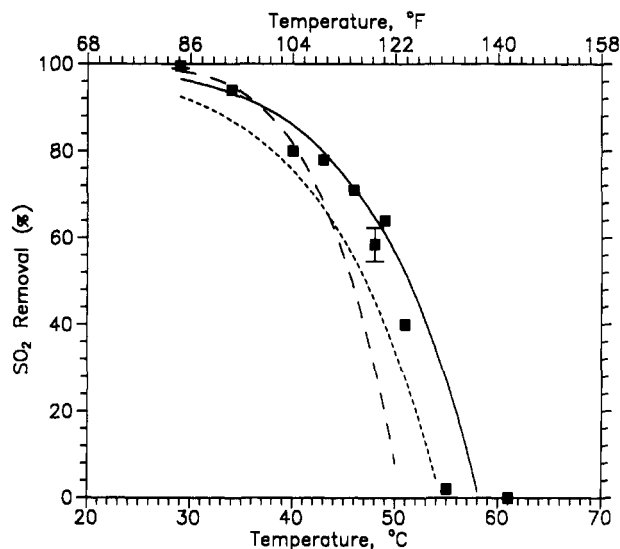

Figure 5. Effect of reaction temperature on SO_2 removal under a moisture content of 2.7% (v/v). The inlet NH_3 and SO_2 concentrations are 6000 and 3000 ppm, respectively: (■) experimental data; (- -) theoretical prediction of assuming the product to be NH_4HSO_3; (- - -) assumes the product to be $(NH_4)_2SO_3$; and (—) assumes products to be an ideal mixture of $(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$.

$((NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O)$ may be possible since the only difference in their chemical structures is the water bond.

Figure 6 shows the experimental results and three theoretical predictions for evaluating the effect of moisture content on the total sulfur removal at a temperature of 51 °C. The NH_3 utilization rates were also measured, and theoretical predictions were made. The results are shown in Figure 7. As can be seen in Figures 6 and 7, the trends
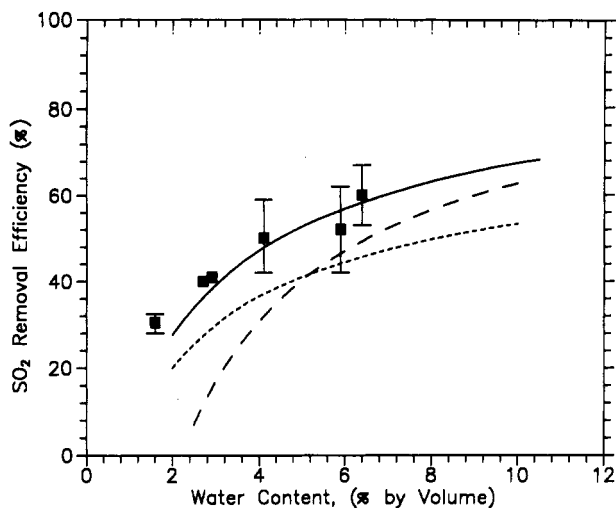
Figure 6. Effect of moisture content on SO_2 removal under a reaction temperature of 51 °C. The inlet NH_3 and SO_2 concentrations are 6000 and 3000 ppm, respectively: (■) experimental data; (– –) theoretical prediction of assuming the product to be $(NH_4)_2SO_3 \cdot H_2O$; (- - -) assumes the product to be $(NH_4)_2SO_3$; and (—) assumes products to be an ideal mixture of $(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$.
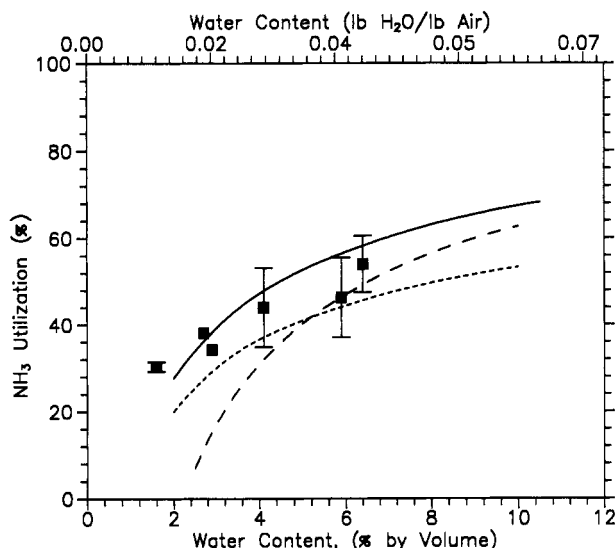

Figure 7. Effect of moisture content on NH_3 utilization under a reaction temperature of 51 °C. The inlet NH_3 and SO_2 concentrations are 6000 and 3000 ppm, respectively: (■) experimental data; (– –) theoretical prediction of assuming the product to be $(NH_4)_2SO_3 \cdot H_2O$; (- - -) assumes the product to be $(NH_4)_2SO_3$; (—) assumes products to be an ideal mixture of $(NH_4)_2SO_3$ and $(NH_4)_2SO_3 \cdot H_2O$.

for SO_2 removal and NH_3 utilization are very similar as moisture content varies. The ratios of the NH_3 utilization to total sulfur removal are close to each other at different moisture contents. The average value is 1.8 with a standard deviation of ±0.15. This observation, together with the results shown previously in Figures 4 and 5, indicates that the NH_3 to SO_2 reaction ratio should be close to 2 at high temperatures. Therefore the three theoretical predictions in Figure 6 are made by assuming the 2:1 sulfites (($NH_4)_2$-SO_3, $(NH_4)_2SO_3 \cdot H_2O$), or an ideal mixture of the two as the main products. The assumption of the ideal mixture of 2:1 sulfites as the product seems to fit the experimental data better than assuming either $(NH_4)_2SO_3$ or $(NH_4)_2$-$SO_3 \cdot H_2O$ as the products. However, comparing these theoretical prediction curves, it is seen that the curve made by assuming an ideal mixture of 2:1 sulfites tends to approach the curve of assuming $(NH_4)_2SO_3$ as the only product at lower moisture contents. This indicates that $(NH_4)_2SO_3$ particles are the dominant products at lower

moisture content conditions. The moisture contents are in large excess of the stoichiometric requirement of forming $(NH_4)_2SO_3 \cdot H_2O$ particles. On the other hand, the $(NH_4)_2$-$SO_3 \cdot H_2O$ particles are the dominant products at high moisture environments. It is also seen that the SO_2 removal increases by about 30% for an increase of the moisture content from 1.6% to 6.4% (v/v). Therefore it may be concluded that moisture content does not affect the product composition greatly, but it plays an important role on the SO_2 removal.

In addition, pH values were also measured at those conditions, and no trend was observed as moisture content varied, with an average value of 7.54 and a standard deviation of ±0.3. Scott and McCarthy (1967) measured the pH value of NH_4HSO_3 to be approximately 4.0 and the pH value of $(NH_4)_2SO_3$ to be approximately 8.0. These further indicate that 2:1 products were dominant during the experiments at 51 °C.

Conclusions

The SO_2 removal by NH_3 injection was studied experimentally. The experimental results were compared with a thermodynamic analysis of several possible reaction schemes. The effects of moisture content and reaction temperature on the SO_2 removal and the compositions of reaction products have been determined. The moisture content in the system played an important role on the sulfur dioxide removal. An increase of the moisture content from 1.6% to 6.4% (v/v) by volume resulted in a 30% increase of the SO_2 removal efficiency at a reaction temperature of 51 °C. This has been verified both from experimental data and the thermodynamic analysis. The NH_3–SO_2–H_2O vapor reactions were favored at low temperatures. An increase in the reaction temperature may result in a significant reduction of the SO_2 removal. The SO_2 removal dropped to zero at temperatures of around 55 °C and a moisture content of 2.7% by volume.

The results of wet chemical analysis showed that the NH_3–SO_2–H_2O vapor reaction products were primary sulfite particles, which may be oxidized to form sulfate particles after being collected on the filter. Ratios of NH_4^+/ SO_4^{2-} by wet chemical analysis as well as pH values of the product solution indicated that the 2:1 ammonium sulfite particles were the dominant products in high-temperature experiments. This is further confirmed by the thermodynamic prediction of the system which assumed an ideal mixture of the 2:1 sulfites as the product.

However, it has not fully explained the reasons for different SO_2 removals observed between pilot-scale tests (Keener and Davis, 1988) and bench-scale results (Stromberger, 1984). In addition to the effects of moisture content and reaction temperature, the catalytic and reactive effects of fly ash on SO_2 removal may be significant in a pilot-scale study. The chemical and physical properties of fly ash have been studied (Reed et al., 1984; Martinez et al., 1991) and utilized to enhance SO_2 removal (Jozewicz et al., 1988; Ho and Shih, 1992). Therefore a further examination of the chemical and physical properties of fly ash on the enhancement of SO_2 removal by NH_3 injection may be encouraged.

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