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Regeneration of FGD Waste Liquors: Production of Ammonium and Potassium Sulfate Mixed Fertilizer

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Table of Contents

Progress Summary	3
Abstract	4
Introduction	5
Experimental	8
Results and Discussion	9
Precipitation of N-S Compounds	9
Hydrolysis of N-S Compounds	12
Summary and Future Study	18
Notations	20
References	21
Figure Captions	26

Progress Summary

July 1993 - Sept. 1993

Based on confirmation of the feasibility of the K_2SO_4 process where a metathetical reaction was performed by adding potassium sulfate to the scrubbing liquor and the crystals formed as a result of the reaction were hydrolyzed to produce ammonium sulfate, detailed experimental investigations continued on precipitation and hydrolysis characteristics of the N-S compounds in the waste scrubbing liquor. In the investigation of precipitation characteristics, amount of removed N-S compounds, precipitated crystals, and the potassium left over in the scrubbing liquor were determined as a function of added K_2SO_4 . In the investigation of the acid-catalyzed hydrolysis of the precipitated N-S compounds to ammonium sulfate was performed under sulfuric acid environment. The completion of this conversion was typically obtainable within 18 hrs at 100 °C and 1M H_2SO_4 acidic environment. The hydrolysis pattern of these precipitated N-S compounds was observed to be nearly the same as that of pure KATS. It was also observed that the hydrolysis of the N-S compounds was little affected by changes in sulfuric acid concentration and initial concentration of the N-S compounds, compared to its strong dependence on temperature. Analysis of the observation also revealed that the overall reaction of the precipitated N-S compounds to ammonium sulfate can be described as first order kinetics in terms of N-S compound concentration.

The observations made so far on precipitation and hydrolysis characteristics of the N-S compounds in the waste scrubbing liquor are summarized for publication in a technical journal.

ABSTRACT

Regeneration of the Fe^{II} -EDTA scrubbing liquors for simultaneous removal of SO_2 and NO_x in flue gas involves removing the nitrogen-sulfur (N-S) compounds accumulated in the liquor. In this paper, we investigated a simple regeneration process which selectively precipitates the N-S compounds as potassium salts and then hydrolyzes them to yield ammonium/potassium sulfate as a marketable byproduct. We believe this is the first report on precipitation and hydrolysis characteristics of the N-S compounds in actual waste scrubbing liquor. Precipitation of the N-S compounds was achieved by adding K_2SO_4 to the scrubbing liquor. Effects of the amount of added K_2SO_4 on the amount of removed N-S compounds, precipitated crystals, and the potassium left over in the scrubbing liquor were studied. Hydrolysis of the precipitated N-S compounds to ammonium sulfate was performed in a sulfuric acid environment. Effects of acidity, concentration of N-S compounds, and temperature on the hydrolysis are discussed. Analysis of the observed hydrolysis pattern showed that the reaction proceeded following first order kinetics in terms of N-S compound concentration.

INTRODUCTION

Conventional flue gas clean up technologies have been used for many years to control SO₂ emission from stationary combustion facilities. Emission levels of NO_x have generally been met through combustion modification techniques. However, emission regulations will become more stringent requiring increased emission control of both NO_x and SO₂. Among a number of options available to remove either SO₂ or NO_x from flue gas, development of integrated processes that remove both SO₂ and NO_x in a single system is of interest. The lime/limestone wet scrubbing process is the most widely used flue gas desulfurization system. This system is efficient in SO₂ removal (more than 90 % SO₂ removal is reported to be easily obtained) (Sloss *et al*, 1992; Martin, 1981, Faucett *et al*, 1977). However, NO_x removal via this system is not efficient because NO, which is the major component of NO_x, is only slightly soluble in aqueous solution. Attempts have been made to achieve a combined SO₂ and NO_x removal system which can be coupled to the lime/limestone desulfurization process. Among the options available for achieving this goal, a simple approach would be the use of an additive to increase the solubility of NO in the scrubbing liquor. Of various types of additives, one which has received much attention is ferrous chelate such as Fe^{II}-EDTA (ferrous ion coordinated to ethylenediaminetetraacetic acid), with which NO is combined to form Fe^{II}-EDTA(NO) and then converted to N₂O, N₂, and nitrogen-sulfur (N-S) compounds by reacting with dissolved SO₂. Extensive investigation has been undertaken on the chemistry and performance of a wet scrubbing system using Fe^{II}-EDTA as an additive (Chang *et al*, 1982; Chang, 1986; Sada *et al*, 1980, 1986, 1988; Yih & Lii, 1989). Several independent tests performed with laboratory scale scrubbing units have shown NO removal of 70 % or more (Sada *et al*, 1986, 1988; John & Livengood, 1989). In spite of this promising performance, this wet process has not yet reached a commercial stage, largely because of economic considerations. However, the economic drawback might be overcome by process improvement.

A flue gas wet scrubbing method generates, in general, the inevitable problem of waste liquor production/treatment. Therefore, a complete scrubbing process should incorporate a regeneration step for the waste liquor. Two characteristic aspects associated with wet scrubbing processes utilizing ferrous chelates as an additive for simultaneous removal of SO_2 and NO_x are gradual oxidation of ferrous ion to inactive ferric ion by residual oxygen in the flue gas and accumulation of N-S compounds in the scrubbing liquor (Sada *et al*, 1980, 1986; Chang, 1986). Therefore, regeneration of scrubbing liquors involves both removing the accumulated N-S compounds and reducing ferric ion back to ferrous ion. Although removal of the N-S compounds from the scrubbing liquor is a key regeneration step, no simple process has yet been reported. In this work, we study a regeneration step which removes the N-S compounds from scrubbing liquors and then converts them to a salable byproduct.

There exist a number of regeneration processes incorporated into simultaneous SO_2 and NO_x wet scrubbing facilities (Martin, 1981, Faucett *et al*, 1977). Although their details may differ depending on types of additives and chemical species accumulated in the scrubbing liquor, they can be classified into two groups based on ultimate schemes of regeneration. One group of processes are characterized as those in which the entire bleed stream from the scrubber is treated with sulfuric acid to decompose the accumulated N-S compounds by hydrolysis (e.g., Chisso Engineering Process and Mitsubshi Heavy Industry Process). Because sulfuric acid is added to the whole scrubbing liquor (mostly water), the process not only requires a significant amount of sulfuric acid to maintain the level of hydrolysis acidity but also is totally destructive of the scrubbing liquor. Therefore, this type of process is probably not economical compared to a process which selectively separates N-S compounds from the scrubbing liquor and performs further treatment only on the separated compounds. The second group of processes are characterized as those where N-S compounds are selectively precipitated and decomposed to yield N_2 (e.g., Asahi

Chemical Process). This process produces no marketable byproduct after the decomposition of the N-S compounds.

A regeneration route under current investigation is designed to possess an advantage over the above-mentioned processes, i.e., it selectively separates N-S compounds from the scrubbing liquor and then converts them to a salable byproduct. Fig. 1 illustrates the regeneration process incorporated into a typical wet scrubbing process which utilizes ferrous chelate for simultaneous removal of SO_2 and NO_x (here, key regeneration stages are denoted in the dotted box). From a bleed of the main scrubbing liquor stream, N-S compounds are separated after converting them to potassium salts by a metathetical reaction with potassium sulfate. Use of potassium sulfate has been suggested from the fact that the potassium salts of N-S compounds possess lower solubility in aqueous solution compared to other types of metal salts (Chang, 1986; Sada *et al*, 1988). The precipitated potassium salts of the N-S compounds are then filtered while the scrubbing liquor is recycled to the main scrubbing liquor stream. Next, the separated potassium salts of the N-S compounds are hydrolyzed in a sulfuric acid environment. Current understanding of reaction pathways suggests a possible end product of the hydrolysis of N-S compounds is NH_4^+ which can be recovered as $(\text{NH}_4)_2\text{SO}_4$ along with regenerated K_2SO_4 . Hydrolysis of N-S compounds is known as an acid catalyzed reaction (Nickless, 1968; Chang *et al*, 1982). Thus sulfuric acid is added to the hydrolyzer as catalyst. After completion of the hydrolysis, the hydrolyzed solution is processed through post-treatment stages of cooling/evaporation, neutralization, etc. to yield ammonium and potassium sulfate crystals as a salable grade of mixed fertilizer.

In the regeneration process described above, precipitation and hydrolysis of N-S compounds are two key stages. Nothing has been reported for the precipitation of N-S compounds. For the hydrolysis of N-S compounds, the few reports available are focused on hydrolysis of specific N-S compound under limiting low concentration and therefore do

not provide direct technical information for practical design (Doyle & Davidson, 1949; Maron & Berens, 1950; Candlin & Wilkins, 1960). In order to demonstrate feasibility of the above regeneration process and to outline practical conditions, we performed an experimental investigation of the precipitation and hydrolysis characteristics of the N-S compounds in actual waste scrubbing liquor. This study is not specific only to the above regeneration process. Either of the stages can be independently incorporated into a number of preexisting regeneration schemes.

EXPERIMENTAL

Experimental investigations were performed to study the precipitation and hydrolysis characteristics of the N-S compounds in Fe^{II} -EDTA waste scrubbing liquor. The waste scrubbing liquor used in the experiment was obtained from Dravo Lime Co. (Pittsburgh, PA) and its approximate composition is listed in Table 1. To precipitate the N-S compounds by a metathetical reaction, a known amount of K_2SO_4 was added to 100 ml of scrubbing liquor and allowed to sit at room temperature for approximately 5 hrs with stirring. No adjustment to liquor pH was made. In measuring the minimum amount of K_2SO_4 required to precipitate the N-S compounds, the onset of precipitation was determined with a light beam by visually examining the Tyndall reflection of fines formed in the liquor. After the metathetical reaction with K_2SO_4 , precipitates were filtered and analyzed for morphology and element composition. Element analysis of samples was performed by Desert Analytics (Tucson, AZ) using a C-H-N Analyser (Perkin-Elmer 240B) for nitrogen, an Elemental Analyzer (Leeman 440) for sulfur, and an Atomic Absorption (Perkin-Elmer 305B) for metals. Hydrolysis of the precipitated N-S compounds to ammonium sulfate was done by dissolving a sample of crystals in an aqueous sulfuric acid solution and heating the liquor. The progression of hydrolysis was

monitored by periodically removing a portion of the liquor and analyzing for the concentration of ammonium ion formed by hydrolysis. The concentration of ammonium ion was measured using an ammonium ion selective electrode (Orion Model 95-12).

To compare characteristics of the precipitated N-S compounds with those of a model N-S compound, pure potassium amine trisulfonate (KATS) and potassium amine disulfonate (KADS) were synthesized following Sisler & Audrieth (1938). The sulfur dioxide gas required to prepare these compounds was obtained from sulfurous acid provided by Fisher Scientific Co. All the other chemicals utilized in the experiment were reagent grade.

RESULTS AND DISCUSSION

Precipitation of N-S compounds

According to previous studies (Chang, 1986; Littlejohn & Chang, 1984; Sada *et al*, 1986), the major N-S compounds in scrubbing liquors are hydroxylamine disulfonic acid $[(\text{HO}_3\text{S})_2\text{NOH}]$, hydroxylamine monosulfonic acid $[(\text{HO}_3\text{S})\text{NHOH}]$, amine trisulfonic acid $[(\text{HO}_3\text{S})_3\text{N}]$, amine disulfonic acid $[(\text{HO}_3\text{S})_2\text{NH}]$, and sulfamic acid $[(\text{HO}_3\text{S})\text{NH}_2]$. These compounds are present as soluble metal salts in neutral or near neutral scrubbing liquor. On addition of potassium sulfate, these compounds undergo metathetical reactions to precipitate as less soluble potassium salts. For example, KADS precipitates by

It is not clear whether all of the N-S compounds can be removed from the scrubbing liquors as potassium salts since typical total concentrations of these N-S compounds are small (less than 300 mMol/liter) (Chang *et al*, 1982; Sada *et al*, 1986). The most probable precipitate will be KADS. KADS has low solubility in aqueous solution (Brauer, 1963;

Nickless, 1968; Sisler & Audrieth, 1938; Diverse & Haga, 1892). Although KATS is more insoluble in aqueous solution than KADS, ATS is unstable in acidic environments and readily decomposes to ADS (Chang *et al*, 1982). Hydroxylamine sulfonic acids react with abundant bisulfite ions and are converted to ADS. In addition, potassium salts of hydroxylamine sulfonic acids have higher solubilities than KADS. Therefore, KADS seems to be the major N-S compound in the potassium salt precipitate.

Fig.2(a) shows a photomicrograph of the precipitated crystals formed by adding K_2SO_4 to scrubbing liquor. These crystals are composed of fine polycrystallites which are quite different in morphology from the added K_2SO_4 crystals, shown in Fig.2(b). When compared with pure KATS and KADS, the morphology of the precipitated crystals was close to that of KADS. To confirm the precipitation of N-S compounds, element analysis was performed for samples of crystals precipitated by adding 5 g K_2SO_4 /100 ml scrubbing liquor. The result is shown in Table 2. The results of nitrogen and sulfur analysis imply that the precipitated crystals are close to KADS, which is consistent with photomicrographic observations.

Since precipitation of N-S compounds with K_2SO_4 was confirmed, we then studied various characteristics of the precipitation. First, we investigated what portion of N-S compounds in the scrubbing liquor can be removed by addition of K_2SO_4 . In order to characterize the quantity, the total amount of N-S compounds in the scrubbing liquor must be determined. Of various elements to be considered in determining the N-S compounds in the scrubbing liquor, nitrogen is of most concern since the element would be representative of the compounds. The total nitrogen content in the scrubbing liquor was determined by element analysis as 0.67 Mol/liter (or 0.84 wt %) of scrubbing liquor. This total nitrogen content included the contribution of nitrogen compounds such as EDTA ($C_{10}H_{16}N_2O_8$) and therefore was greater than the nitrogen content by N-S compounds. Hydrolyzable nitrogen content is determined by measuring the ammonium ion concentration after

completely hydrolyzing the mother liquor in a 1 molar sulfuric acid environment. Since EDTA was observed not to be hydrolyzable under the same acidic condition, the hydrolyzable nitrogen content is representative of N-S compounds in the scrubbing liquor. The hydrolyzable nitrogen content in the scrubbing liquor was measured as 0.38 M/liter. Fig.3 shows dependence of the fraction of N-S compounds removed from the scrubbing liquor has a function of added K_2SO_4 . Up to 2.8 g K_2SO_4 /100 ml liquor, no precipitation was observed and all the N-S compounds remained in the scrubbing liquor. As the amount of added K_2SO_4 increased, there was a sharp increase in the amount of N-S compounds removed from the scrubbing liquor. However, this increment of removed N-S compounds decreased with the amount of added K_2SO_4 . When the addition of K_2SO_4 reached 12.5 g/100 ml liquor, approximately 50 % of the N-S compounds in the scrubbing liquor were removed. Further addition of K_2SO_4 had little effect.

In Fig.4, dependence of precipitated crystals on the amount of added K_2SO_4 is shown as an open symbol curve. As the amount of added K_2SO_4 increases, the total amount of precipitated crystals increases. As a quantitative measure of N-S compounds in the precipitates, we used the amount of KADS equivalent, calculated as the amount of KADS in terms of hydrolyzable nitrogen content in the precipitates. The fraction of KADS equivalent in the precipitate vs. the amount of added K_2SO_4 is presented as the filled symbol curve in Fig.4. As the addition of K_2SO_4 increased, the fraction of KADS equivalent decreased. As more K_2SO_4 is added, more compounds other than N-S compounds precipitate. In addition to unreacted K_2SO_4 , a significant amount of magnesium compounds (magnesium sulfate) were observed to be contained in the precipitates.

In Figs. 3 and 4, precipitation characteristics were described based on total amount of added K_2SO_4 . The potassium ions remaining in the scrubbing liquor after the precipitation will be recycled to the scrubber and therein much of them will be lost as

entrainment in gypsum product. Therefore, it is important to determine how much potassium ion added as K_2SO_4 remains in the scrubbing liquor. Fig.5 shows a plot of the added K_2SO_4 vs. the fraction of the added potassium which remains in the scrubbing liquor. Up to the addition of 2.8 g K_2SO_4 /100 ml liquor, no precipitation was observed and all the added potassium remained in the scrubbing liquor. As more K_2SO_4 is added, the portion remaining in the scrubbing liquor monotonically decreased. This implies that although the absolute amount of potassium ion remaining in the scrubbing liquor increases with the amount of added K_2SO_4 , a larger increment occurs in the precipitates which may be in the form of potassium salts of N-S compounds and undissolved K_2SO_4 . In Fig.5, it is notable that more than 60 % of the added potassium remains in the scrubbing liquor. This observation indicates that loss of the dissolved potassium, probably as entrainment on the gypsum precipitates, is a serious detriment to the economy of the type of regeneration process described in Fig.1.

Hydrolysis of N-S compounds

The reaction chemistry involved in hydrolysis of various N-S compounds is available in references (Chang *et al*, 1982; Nickless, 1968). In view of the reaction chemistry, conversion of precipitated KATS and KADS to ammonium sulfate may be achieved by the following routes. ATS is hydrolyzed to ADS by

This acid-catalyzed reaction is reported to rapidly occur even in a neutral solution and 25 °C (Sisler & Audrieth, 1938; Chang *et al*, 1982). ADS is hydrolyzed irreversibly and quantitatively to yield sulfamate as follows (Doyle & Davidson, 1949).

Sulfamate is known to undergo hydrolysis to form ammonium and sulfate ions by a mechanism involving a pre-equilibrium between sulfamate ion and sulfamic acid, followed by slow hydrolysis of the acid (Maron & Berens, 1950; Candlin & Wilkins, 1960; Hughes & Lusty, 1977):

From the mechanisms of hydrolysis, it is difficult to describe hydrolysis of N-S compounds precipitated from the scrubbing liquor in terms of reagents since the precipitates contain various species of N-S compounds at different concentration. Here we note that ammonium ion is an end product which is formed only from decomposition of the N-S compounds by hydrolysis. Thus concentration of the ammonium ion in a hydrolyzed crop can be used as a measure of overall hydrolysis. In order to characterize the progression of hydrolysis, we define extent of hydrolysis, $x_{\text{NH}_4^+}$, as the ratio of the existing ammonium ion concentration, $C_{\text{NH}_4^+}$, to ammonium ion concentration at completion of hydrolysis, $C_{\text{NH}_4^+, \infty}$. This definition was made since the goal of hydrolysis was converting the precipitated N-S compounds to ammonium sulfate regardless of formation of intermediate species. Therefore, the extent of hydrolysis is calculated as

$$\text{Extent of hydrolysis, } x_{\text{NH}_4^+} = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_4^+, \infty}} \quad (5)$$

Here, the concentration of ammonium ion at completion of hydrolysis is implicitly related to the total concentration of N-S compounds before hydrolysis. This relation seemed reasonable since our laboratory test showed that pure KATS was hydrolyzed to form ammonium ion stoichiometrically.

Before investigating various effects of hydrolysis conditions on conversion of precipitated N-S compounds, we used pure KATS as a model N-S compound for

understanding hydrolysis characteristics. The extent of hydrolysis vs. time plot obtained for KATS at 100 °C and 1 M H_2SO_4 is presented as a solid line in Fig.6. In the plot, it is shown that before hydrolysis, no ammonium ion was present in the reaction mixture and as hydrolysis progressed, the concentration of ammonium ion increased and reached a fixed value at complete conversion. Under the strong acidic environment investigated, completion was typically attained within 18 hrs. For purpose of comparison, N-S compounds precipitated with 10 g K_2SO_4 /100 ml liquor were converted under the same hydrolysis conditions. This result is presented in Fig.6. The hydrolysis trend obtained for the precipitated N-S compounds was observed to be nearly the same as that of KATS. This seems to occur since hydrolysis of KATS to KADS, given by eq.(1) is so rapid, as pointed out by Sisler & Audrieth (1938), that the overall rate of hydrolysis to ammonium sulfate gave no significant difference between the pure KATS and the precipitated crystals whose major component is KADS.

Hydrolysis of N-S compounds to ammonium sulfate is known to be an acid-catalyzed reaction (Chang *et al*, 1982; Nickless, 1968). Thus we investigated the effect of sulfuric acid concentration on hydrolysis of precipitated N-S compounds and presented the result in Fig.6. As the concentration of sulfuric acid increased from 0.5 to 2 M/liter, the rate of hydrolysis was observed to increase slightly. Changes in sulfuric acid concentration involves two aspects on rate of hydrolysis. Increase in the acid concentration on one hand can accelerate the hydrolysis by increasing concentration of hydrogen ion. On the other hand it decreases the rate by reducing the activity of water molecules which should be incorporated as a hydrolysis reactant. The observed slight increase in hydrolysis rate with concentration of sulfuric acid implies that the two effects are competitive in the investigated acidity range. This point is comparable with the observation of Hughes and Lusty (1977) on hydrolysis of sulfamic acid catalyzed by HClO_4 . According to their report, hydrolysis rate increased with increasing the HClO_4 concentration up to 1.27 M/liter and kept nearly constant up to 4.9 M/liter. Thereafter, further increase in the acid concentration resulted in

reducing the hydrolysis rate. Considering one mole of H_2SO_4 corresponds to two moles of HClO_4 in terms of hydrogen ion, our observation seems to be consistent with Hughes and Lusty (1977). In addition, hydrolysis trends shown in Fig.6 would not greatly differ from that of maximum hydrolysis rate obtainable via acidity change.

Fig.7 shows effects of concentration of precipitated N-S compounds on hydrolysis. As the concentration of N-S compounds increased from 0.2 to 1 M/liter, extent of hydrolysis achieved within 5 hrs decreased slightly. For all the cases, however, complete conversion to ammonium sulfate was obtained within 18 hrs. The slightly decreased hydrolysis rate at higher N-S compound concentration seems to result since the activity of water molecules is reduced at the higher reactant concentration. It may also occur as the relative concentration of sulfuric acid to N-S compounds decreased. If deviation by these effects are taken into account, the observed extent of hydrolysis may show insensitiveness relative to initial concentration of N-S compounds. Here we note that insensitiveness of extent of reaction to initial reactant concentration is a typical characteristic of first order irreversible reactions (Levenspiel, 1962). Thus, the overall kinetics for conversion of N-S compounds to ammonium sulfate, which covers all the steps in eqs. (1) - (4), may be simply put as a first order irreversible reaction in terms of concentration of N-S compounds:

$$\frac{d}{dt} C_{\text{NH}_4^+} = - \frac{d}{dt} C_{\text{N-S}} = k C_{\text{N-S}} f(C_{\text{H}^+}, \dots) \quad (6)$$

where $C_{\text{N-S}}$ is concentration of N-S compounds, k is a rate constant, C_{H^+} is concentration of hydrogen ion, and f is a function which is mainly dependent on C_{H^+} . Here, we implicitly used $C_{\text{NH}_4^+} + C_{\text{N-S}} = C_{\text{NH}_4^+, \infty} = \text{constant}$. The kinetic expression in eq.(6) is not unrealistic since previous studies showed that each step of the hydrolysis given by eqs.(1), (2), and (3) & (4) follows first order kinetics.

Fig.8 shows effects of temperature on the hydrolysis of precipitated N-S compounds. At 80 °C, the extent of hydrolysis slowly increased with elapse of time to reach less than 90% after 18 hrs, while at 100 °C it increased exponentially to reach completion within that time. This observation implies that temperature plays a significant role in hydrolysis and elevated temperature will reduce the required space time in a practical process. In order to obtain a quantitative description of the hydrolysis, we further analyze the temperature dependence, presented in Fig.8, in terms of kinetics. Assuming that the variation in ionization of sulfuric acid is small enough within the narrow temperature range, f in eq.(6) would be nearly constant. The given kinetic expression is then integrated to yield

$$\ln \left(\frac{C_{N-S}}{C_{NH_4^+}} \right) = \ln (1 - x_{NH_4^+}) = -kft \quad (6)$$

This expression shows that if hydrolysis of N-S compounds follows the first order kinetics given by eq.(6), $\log(1-x_{NH_4^+})$ vs. time plot will yield a straight line, with its slope proportional to the rate constant. Fig.9 shows the $\log(1-x_{NH_4^+})$ vs. time plot for the data presented in Fig.8. In the plot, data collected at fixed temperature were shown to be well represented by a straight line. This supports the hypothesis that hydrolysis of precipitated N-S compounds to ammonium sulfate follows first order kinetics and is consistent with the observation of insensitive hydrolysis on initial concentration of N-S compounds. From temperature-dependent slopes in Fig.9, activation energy is obtained using the Arrhenius equation, i.e., $k = k_0 \exp (-E/RT)$. From the $\ln k$ vs. $1/T$ plot, presented in Fig.10, activation energy of the hydrolysis was estimated as 25.0 kcal. In previous studies, activation energy was obtained as 23.5 kcal for the reaction of eq.(2) (Doyle and Davidson, 1949) and 30.5 kcal for a combination of eqs.(3) and (4) (Maron and Berens, 1950). We estimated the activation energy for the overall hydrolysis to ammonium sulfate and thus it may not be directly compared with the reported values of constituent steps. However, it is remarkably consistent, in order of magnitude, with the values of intermediate steps. This

result supports the validity of our interpretation which will be useful in the practical design of regeneration processes.

After completion of hydrolysis, ammonium and potassium sulfates can be crystallized from a hydrolysis crop through a cooling and evaporation combined process. Fig.10 shows a photomicrograph of crystals obtained by evaporating a hydrolysis crop of the potassium salts of N-S compounds precipitated by addition of 5 g K_2SO_4 /100 ml scrubbing liquor. It is difficult to identify individual salts from the morphology shown in the photomicrograph. An element analysis of these crystals showed that the potassium and nitrogen content of these crystals was 24.8 and 4.3 wt %, respectively. As shown in Table 3, when compared with KADS (note that the precipitates of N-S compounds used for hydrolysis were close to KADS), the crystals obtained after hydrolysis are lower in absolute values of potassium and nitrogen content. However, it is notable that the weight ratio of potassium to nitrogen content was conserved after hydrolysis. This observation suggests that the crystals obtained from the hydrolysis crop are ammonium and potassium salts which possess relatively lower content of the species, such as bisulfate salts. In this sense, we consider two ideal cases for the crystals obtained from the hydrolysis crop: bisulfate salts and sulfate salts. 1 mole KADS is composed of 2 mole potassium and 1 mole nitrogen atoms. Thus, hydrolysis of 1 mole KADS can yield, in terms of nitrogen and potassium contents, a mixture of { 1 mole K_2SO_4 + 0.5 mole $(NH_4)_2SO_4$ } or { 2 mole $KHSO_4$ + 1 mole $(NH_4)HSO_4$ }. Theoretical element composition of these two ideal mixtures are presented in Table 3. Both potassium and nitrogen composition of the crystals from the hydrolysis crop ranged between the values of sulfate salts and bisulfate salts, suggesting that the composition of the crystals actually obtained after hydrolysis are close to a mixture of ammonium/potassium sulfate and bisulfate salts. An investigation of X-ray diffraction patterns of the crystals in Fig.10 revealed that the crystals are composed of various kinds of bisulfate salts such as $K_3H(SO_4)_2$, $K_2(NH_4)H(SO_4)_2$, $(NH_4)HSO_4$, etc. This is contrasting with the result of element analysis of the crystals.

SUMMARY AND FUTURE STUDY

We described a simple regeneration scheme of waste scrubbing liquors for simultaneous removal of SO_2 and NO_x in flue gas. To demonstrate the feasibility of the process and to outline practical conditions, precipitation and hydrolysis characteristics of the N-S compounds were investigated using actual waste Fe^{II} -EDTA scrubbing liquor. Precipitation of the N-S compounds was achieved by crystallizing them as less soluble potassium salts after a metathetical reaction with added potassium sulfate. Analysis of the precipitates in morphology and element composition revealed that the precipitate is close to KADS. Amount of removed N-S compounds, precipitated crystals, and the potassium left over in the scrubbing liquor were also determined as a function of added K_2SO_4 . These results showed that addition of 12.5 g K_2SO_4 /100 ml liquor could achieve approximately 50 % removal of the N-S compounds from the scrubbing liquor. It was also shown that more than 60 % of the added potassium is left in the scrubbing liquor after the precipitation.

The acid-catalyzed hydrolysis of the precipitated N-S compounds to ammonium sulfate was performed under sulfuric acid environment. The completion of this conversion was typically obtainable within 18 hrs at 100 °C and 1M H_2SO_4 acidic environment. The hydrolysis pattern of these precipitated N-S compounds was observed to be nearly the same as that of pure KATS. It was also observed that the hydrolysis of the N-S compounds was little affected by changes in sulfuric acid concentration and initial concentration of the N-S compounds, compared to its strong dependence on temperature. Analysis of the observation also revealed that the overall reaction of the precipitated N-S compounds to ammonium sulfate can be described as first order kinetics in terms of N-S compound concentration.

Up to the present, we focused on developing the K_2SO_4 process using potassium sulfate to precipitate N-S compounds in the scrubbing liquor. However, the K_2SO_4

process may not be advantageous because more than 60 % of the added potassium was observed to be left in the scrubbing liquor after the precipitation and loss of the dissolved potassium, probably as entrainment on the gypsum precipitates, is a serious detriment to the economy of the regeneration process. Therefore, we will change research phase and put an emphasis on the development of the lime/limestone process described in our second quarterly report.

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Notations

- C_{H^+} : Concentration of hydrogen ion.
 $C_{NH_4^+}$: Concentration of ammonium ion in a hydrolysis solution.
 $C_{NH_4^+, \infty}$: Concentration of ammonium ion at completion of hydrolysis.
 C_{N-S} : Concentration of N-S compounds.
 E : Activation energy.
 f : An arbitrary function which mainly depends on the concentration of hydrogen ion.
 k : Rate constant.
 k_0 : Pre-exponential factor of the rate constant, k .
 R : Ideal gas constant.
 T : Temperature.
 t : Time
 $x_{NH_4^+}$: Extent of hydrolysis defined as $C_{NH_4^+} / C_{NH_4^+, \infty}$

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Table 1 Typical composition and physical properties of the waste liquor provided by Dravo Lime Co.

Compounds	Concentration
MgSO ₄ /MgSO ₃	~ 10,000 ppm
N-S compounds	~ 5,000 ppm
CaSO ₄ /CaSO ₃	~ 1,000 ppm
Na ₂ SO ₄	~ 1,000 ppm
FeSO ₄ / EDTA	~ 3,000 ppm
pH	6.5 ~ 7.0
Density	1.11 g/cm ³
Viscosity	1.48 cP

Table 2 Results of element analysis for the crystals precipitated with K_2SO_4 .

Compounds		M.W.	Elements (wt %)		
			K	N	S
Theo.	KSO_3NHSO_3K (KADS)	253.3	30.8	5.5	25.3
	$N(SO_3K)_3 \cdot 2H_2O$ (KATS)	407.5	28.8	3.4	23.6
	K_2SO_4	174.3	44.9	-	18.4
Exp.	sample I			5.3	
	sample II		28.0	5.9	23.7

Table 3 Results of element analysis for the crystals obtained after completion of hydrolysis.

Compounds or Mixture		elements (wt %)		K/N weight ratio
		K	N	
Exp.	Crystals from a hydrolysis crop	24.8	4.3	5.8
Theo.	$\text{KSO}_3\text{NHSO}_3\text{K}$ (KADS)	30.8	5.5	5.6
	1 mol K_2SO_4 + 0.5 mol $(\text{NH}_4)_2\text{SO}_4$	32.6	5.8	5.6
	2 mole KHSO_4 + 1 mol $(\text{NH}_4)\text{HSO}_4$	20.2	3.6	5.6

Figure Captions

Fig.1 Illustration of the regeneration process for a typical FeII-EDTA wet scrubbing process.

Fig.2 Photomicrographs of the crystals precipitated from the scrubbing liquor and other standard compounds.

Fig.3 Fraction of N-S compounds removed by precipitation vs. amount of added K_2SO_4 .

Fig.4 Amount of precipitated crystals and fraction of N-S compounds in the precipitates vs. the amount of added K_2SO_4 .

Fig.5 Fraction of the added potassium which remains in the scrubbing liquor vs. the amount of added K_2SO_4 . More than 60 % of added potassium remains in the scrubbing liquor after precipitation of N-S compounds as potassium salts. This observation indicates that loss of the potassium, probably as entrainment of the gypsum precipitates will be significant.

Fig.6 Typical hydrolysis trend of KATS and effects of sulfuric acid concentration on the hydrolysis of precipitated N-S compounds.

Fig.7 Dependence of hydrolysis on initial concentration of precipitated N-S compounds.

Fig.8 Effect of temperature on hydrolysis of precipitated N-S compounds.

Fig.9 $\log(1-x_{NH_4})$ vs. time plot for the data presented in Fig.8

Fig.10 $\ln k$ vs. $1/T$ plot.

Fig.11 photomicrograph of ammonium and potassium sulfates crystallized from a hydrolyzed liquor.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

Fig.11

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