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Project Summary

Ammonium Sulfate and Bisulfate Formation in Air Preheaters

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Nitrogen oxide (NOₓ), emissions from electric utility boilers may be reduced by 80-90 percent, through the application of pollution control technology based on the selective catalytic reduction of NOₓ with ammonia; however, some unreacted ammonia may be emitted from the control system. This study investigated the potential impact of these ammonia emissions on a combustion air preheater, downstream of a selective catalytic reduction system. A thermodynamic analysis was conducted which indicated that both ammonium sulfate $((NH_4)_2SO_4)$ and ammonium bisulfate (NH_4HSO_4) could form in the intermediate and low temperature zones of an air preheater and that $(NH_4)_2SO_4$ was the thermodynamically favored reaction product. A kinetic analysis of the NH_3-SO_3 reactions was conducted which showed that $NH_4 HSO_4$ is the first compound formed under the time-temperature histories in an air preheater. This indicates that the reaction which forms NH_4HSO_4 from gaseous reactants is more rapid than that which forms $(NH_4)_2SO_4$. The study identified five techniques for minimizing the deposition of ammonium sulfates in an air preheater. A technical and economic evaluation of each solution was conducted: the results indicate that the use of available air preheater design options is the optimum technique for minimizing deposit formation.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Currently, the principal methods of controlling nitrogen oxide (NOₓ) emissions from stationary combustion sources are combustion modifications and flue gas treatment. Combustion modifications are employed on new utility boilers and are generally capable of reducing NOₓ emissions up to 50 percent. Flue gas treatment is a technology which is used commercially in Japan and it is being applied on a limited basis in the U.S.

Several flue gas treatment processes have been developed in Japan. Of these, only selective catalytic reduction (SCR) of NOₓ with ammonia has commercially demonstrated the capability of limiting NOₓ emissions from stationary sources by 90 percent or more. Because SCR can attain such high NOₓ reduction efficiencies, it is receiving increased attention in the U.S.

For a utility application of SCR, a catalytic reactor is located between the economizer and air preheater sections of the boiler. At this point, ammonia, injected into the flue gas upstream of the catalyst, reacts with NOₓ on the

catalyst surface to form elemental nitrogen and water. The overall reactions can be represented by:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$
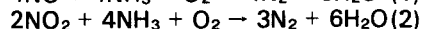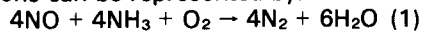
Although SCR systems have undergone extensive commercial development in Japan, an unresolved issue is that of ammonia emissions from the process and the impact of these emissions on equipment downstream of the catalytic reactor. Such equipment can include air preheaters and other pollution control equipment. This study specifically addresses the impact of ammonia emissions on the operation of air preheaters downstream of SCR systems.

Study Objectives and Approach

This study had three major objectives: (1) to collect and interpret data on the thermodynamics and kinetics of NH_3-SO_3 reactions; (2) to identify techniques for minimizing the deposition of ammonium sulfates in an air preheater; and (3) to complete a technical and economic evaluation of those techniques.

The approach used to meet the study objectives began with a thermodynamic analysis of possible NH_3 reactions to identify conditions which favor the formation of ammonium sulfates. Experimental data were then compared to the expected equilibrium results and a kinetic model was developed to predict the formation and deposition of ammonium sulfates.

Information was also collected on air preheater design and operation. These data were then used, in conjunction with the results of the thermodynamic and kinetic analyses, to identify techniques for minimizing the deposition of ammonium sulfates in an air preheater. Finally, a technical and economic evaluation of each technique was completed.
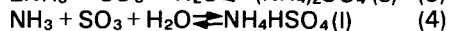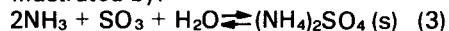
Problem Definition

The problem of ammonium sulfate deposition has several aspects which must be defined before solutions can be identified. The chemistry of the NH_3-SO_3 reactions must be examined and the principal causes of deposit formation pinpointed. In addition, the impact on operation and maintenance of the air preheater and the environmental impacts associated with $(NH_4)_2SO_4$/NH_4 HSO_4 deposition must be considered.

NH₃-SO₃ Chemistry

Experience at SCR installations has demonstrated that NH_3 and SO_3 can react and deposit in air preheaters. Chemical analysis of the deposits indicates that the principal reaction products are $(NH_4)_2SO_4$ and NH_4HSO_4. Other components in the deposits include corrosion products (NH_4-Fe-SO_4 compounds) and fly ash (Ca, Si, and Al compounds). The following discussion identifies reactions which can occur in an air preheater.[1, 2, 3.]

The NH_3-SO_3 reactions which can take place in an air preheater are illustrated by:

$$2NH_3 + SO_3 + H_2O \rightleftharpoons (NH_4)_2SO_4 \text{ (s)} \quad (3)$$
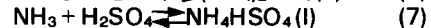$$NH_3 + SO_3 + H_2O \rightleftharpoons NH_4HSO_4 \text{ (l)} \quad (4)$$

These reactions can occur as a gas containing NH_3, SO_3, and H_2O is cooled. For a flue gas stream, the exact temperature at which solid/liquid products begin to form or "condense" depends on the reaction product(s) formed and on the concentration of NH_3, SO_3, and (to a lesser degree) H_2O. In general, as the concentrations of reactants in the gas increase, the temperature at which deposits will form also increases.

Another reaction which occurs as the gas is cooled is represented by:

$$H_2O + SO_3 \rightleftharpoons H_2SO_4 \text{ (g)} \quad (5)$$
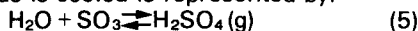
Formation of H_2SO_4 lowers the concentration of SO_3 available for the reaction with NH_3 (Equations 3 and 4.) This, in turn, reduces the temperature at which either $(NH_4)_2SO_4$ or NH_4HSO_4 will form. Of course, NH_3 can react with H_2SO_4 as illustrated by:

$$2NH_3 + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4 \text{ (s)} \quad (6)$$
$$NH_3 + H_2SO_4 \rightleftharpoons NH_4HSO_4 \text{ (l)} \quad (7)$$

However, these reactions occur at a lower temperature than those of NH_3 with SO_3. As a result the formation temperatures for the reactions with H_2SO_4 define a lower limit for formation of $(NH_4)_2SO_4$ and NH_4HSO_4, while the formation temperatures for the reactions with SO_3 define an upper limit.

Based on evaluation of NH_3-SO_3 reactions, the compounds which can form in an air preheater are $(NH_4)_2SO_4$ and NH_4HSO_4. If only $(NH_4)_2SO_4$ forms, it will exist as a solid. This compound does not melt; it decomposes. If NH_4HSO_4 or both compounds form, the deposit may be either solid or liquid, depending on the deposit composition and the temperature as shown in Figure 1.[3, 4]

Ammonium Sulfates and Air Preheater Design

Early experience with corrosion and plugging of air preheaters resulted from condensation of H_2SO_4 vapor on the metal surfaces in the preheater. The deposition of NH_3-SO_3 compounds is somewhat analogous to the H_2SO_4 condensation problem. Liquid NH_4HSO_4 or a solution of $(NH_4)_2SO_4$ and NH_4HSO_4 can condense and deposit in the air preheater. Formation of solid $(NH_4)_2SO_4$ should not present a problem since the solid should not adhere to the surface as

A - Solid $(NH_4)_2SO_4$ and NH_4HSO_4

B - Solid NH_4HSO_4 and Liquid Solution of $(NH_4)_2SO_4$ and NH_4HSO_4

C - Solid $(NH_4)_2SO_4$ and Liquid Solution of $(NH_4)_2SO_4$ and NH_4HSO_4
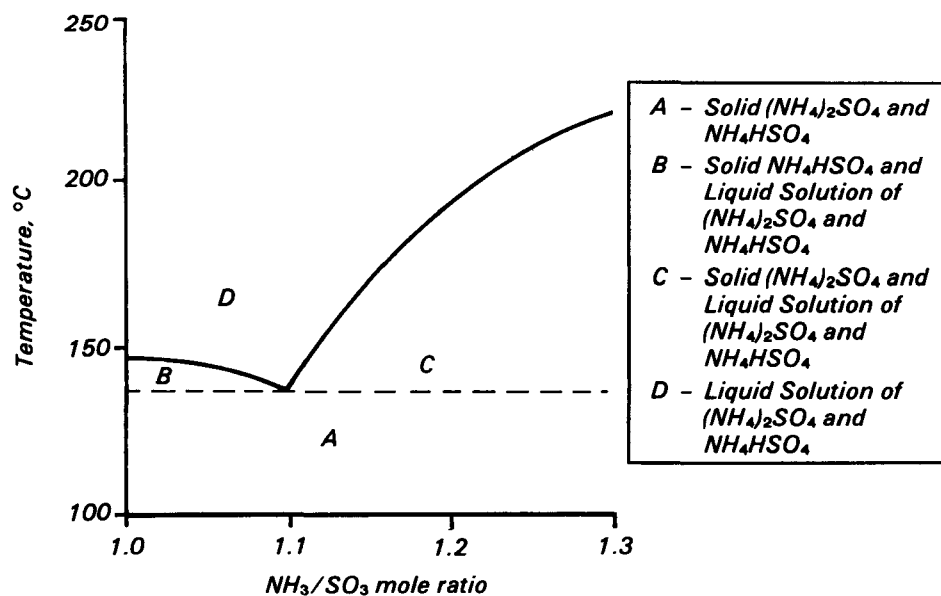
D - Liquid Solution of $(NH_4)_2SO_4$ and NH_4HSO_4

Figure 1. Melting point of NH_3/SO_3 mixtures as a function of composition.

readily as a liquid. However, liquid $(NH_4)_2SO_4/NH_4HSO_4$ deposits can present problems. They tend to collect fly ash particles and to react with both the fly ash and the metal surface in the air preheater to form a solid deposit.

Deposition of ammonium sulfates presents a more significant problem than H_2SO_4 deposition. To understand why, it is necessary to examine the basics of air preheater operation. Most utility boilers employ regenerative air preheaters in which heat is absorbed from the flue gas by metal heat transfer elements. These metal elements are then exposed to the combustion air where they release the heat absorbed from the flue gas. Subsequently, the elements are re-exposed to the flue gas, and the cycle is repeated.

During the heat transfer cycle in a regenerative preheater, the temperature of the metal heat transfer elements changes continuously as they are alternately exposed to flue gas and combustion air. Figure 2 is a typical temperature profile for a regenerative air preheater. The center line represents the average metal temperature as a function of depth through the preheater. The left- and right-hand lines represent the low and high metal temperatures, respectively.[5].

Some features of regenerative air preheaters which are used to minimize the impacts of H_2SO_4 condensation/ plugging include soot blowers and water washing equipment. Soot blowing has been used as an effective technique for controlling and minimizing deposits. Soot blowers direct a high pressure stream of either steam or air onto the heat transfer elements where deposits can accumulate. This dislodges the deposits which are then entrained by the flue gas.

Water washing is usually required to supplement soot blowing of the air preheater. Typically, washing is restricted to boiler outages. However, the frequency of water washing is ultimately determined by the pressure drop across the air preheater. Once the pressure drop increases beyond a certain level, washing is required.

The temperature profile shown in Figure 2 indicates some additional design features used to minimize air preheater plugging and corrosion. As shown, the fluctuation of metal temperatures in the extreme cold end of the air preheater is less than that in the higher temperature zones. This tends to limit H_2SO_4 condensation to the cold end and is due to the design of the heat transfer
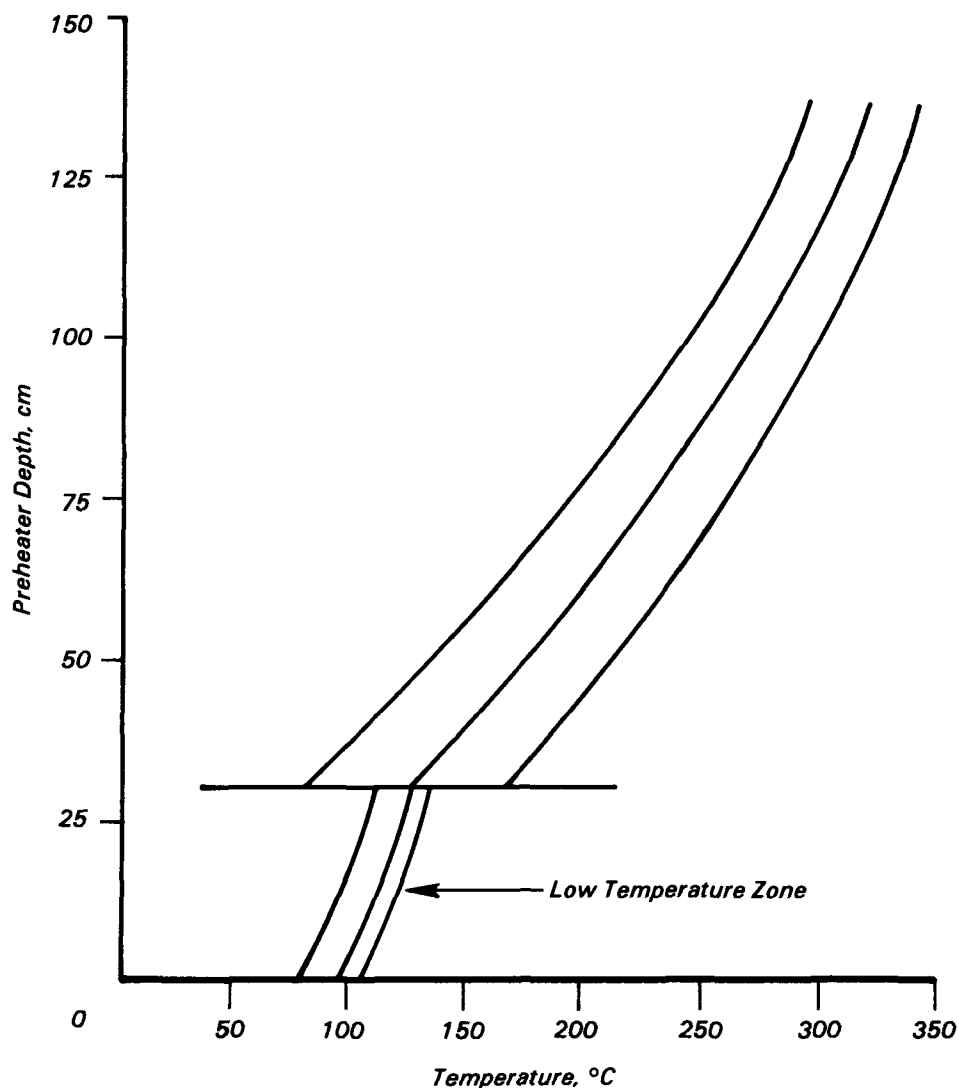

Figure 2. Temperature profile of heat transfer elements in a regenerative air preheater.

elements in the cold end. The cold-end heat transfer elements are constructed of heavy-gauge material which allows the elements to corrode and still retain the strength to withstand the soot blower blast. In addition, the configuration of the elements is different, consisting of spaced, flat sheets oriented parallel to the gas flow. This permits better penetration of the soot blower jet into the cold end. [5, 6] These differences result in the cold-end elements having a higher heat capacity and lower heat transfer efficiency which in turn limits temperature fluctuations.

As previously discussed, the deposition of ammonium sulfates is analogous to H_2SO_4 condensation in an air preheater. However, ammonium sulfates condense at higher temperatures than does H_2SO_4, presenting significant problems. Figure 3 illustrates the relationship between typical $H_2SO_4(l)$, $(NH_4)_2SO_4$, and NH_4HSO_4 initial formation temperatures and the air preheater temperature profile from Figure 2. As shown, H_2SO_4 can form in about 35 percent of the preheater but only the extreme cold-end metal temperatures are always below the acid dewpoint. On the other hand, $(NH_4)_2SO_4$ and NH_4HSO_4 can form in about 50 percent of the air preheater. In this case, some portion of the heat transfer elements in the intermediate zone of the preheater are always below the formation temperatures for ammonium sulfates.
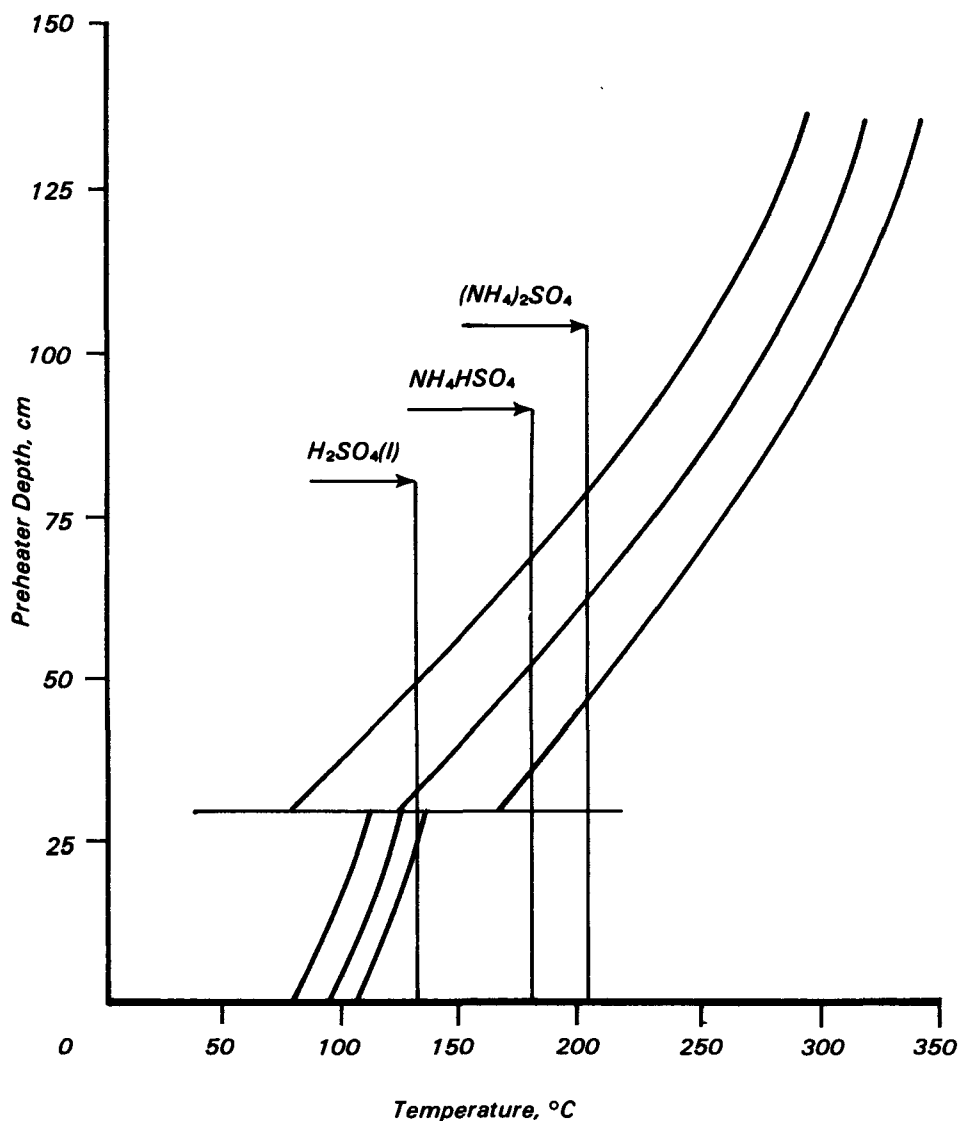
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Figure 3. Preheater Depth, cm (y-axis): 150, 125, 100, 75, 50, 25

Curve labels: $(NH_4)_2SO_4$, NH_4HSO_4, $H_2SO_4(l)$

Temperature, °C (x-axis): 0, 50, 100, 150, 200, 250, 300, 350

Figure 3. $(NH_4)_2SO_4$, NH_4HSO_4, and $H_2SO_4(l)$ formation temperatures in an air preheater.

The fact that both $(NH_4)_2SO_4$ and NH_4HSO_4 can form and deposit in the intermediate temperature zone of an air preheater presents several problems: (1) the heat transfer elements in the intermediate temperature zone are especially susceptible to corrosion since they are typically manufactured from light-gauge carbon steel; (2) soot blowing equipment is not as effective in removing NH_3-SO_3 deposits as it is in removing H_2SO_4 deposits (the blowers are at the ends of the preheater, while NH_3-SO_3 deposits can form in the center); and (3) since soot blowing will probably not be effective in controlling deposit formation in the intermediate zone, water washing may be required more frequently (this could require either forced boiler outages or periodic reductions in boiler load to permit washing and thereby maintain acceptable air preheater performance).

Available data from installations in Japan indicate that air preheater plugging problems do occur. In some cases, soot blowing is ineffective and more frequent water washing is required.[1, 2, 3]

Impact of Deposit Formation on Air Preheater Performance

Two major aspects of air preheater performance can be affected by the deposition of ammonium sulfates thermal efficiency and pressure drop Thermal efficiency, a measure of the heat transferred from the flue gas to the combustion air, is significant since a decline in efficiency (evidenced by an increase in flue gas temperature at the air preheater exit) decreases boiler efficiency.

The impact of $(NH_4)_2SO_2$/NH_4HSO_4 deposition on the thermal efficiency of the air preheater is not expected to be significant. The results of tests conducted by the Electric Power Development Company (EPDC) in Japan showed no evidence of a decline in the thermal efficiency of the preheater.[7] In addition, another study reported that the presence of soot and fly ash deposits can improve the thermal efficiency of the air preheater. This is a result of the deposits actually increasing the heat capacity of the air preheater.[8]

Pressure drop through the air preheater is also an important aspect of preheater performance. An increase in pressure drop through the preheater can cause a slight decline in the thermal efficiency of the boiler. In addition, if the increase is too large, the fans may not be able to maintain full flow rates and the boiler would have to operate at reduced load or be shut down to permit washing of the preheater.

Japanese experience has shown that $(NH_4)_2SO_4$/NH_4HSO_4 deposition can have an adverse impact on the pressure drop through the preheater. In some cases the air preheater pressure drop has increased despite the use of soot blowing, and more frequent water washing of the preheater has been required.

Environmental Considerations

Ammonia emitted from SCR systems can affect operation of downstream equipment and may also have some environmental impacts. The principal environmental impact which is expected to result from deposition of $(NH_4)_2SO_4$/NH_4HSO_4 will be associated with the water stream which is used to wash deposits from the preheater. This stream can contain dissolved, NH_4^+, SO_4^{-2}, $Fe^{+2/3}$, and other compounds which may be present in fly ash. The actual composition of the wash water will be similar to the composition of water from conventional air preheater washing. The principal difference is the presence of NH_4^+ and possibly higher Fe concentrations than normal.

Air preheater wash water is classified as a metal cleaning waste; as such, it must meet the discharge limits which are shown in Table 1.[9] This waste stream can be treated separately or it may be combined with other metal cleaning wastes in a single treatment facility. The type of treatment employed is site specific.

Typically, metal cleaning wastes contain copper and iron; depending on the cleaning process used, significant amounts of NH_3 also may be present. Some typical boiler cleaning chemicals include ammoniated citric acid, ammoniated EDTA, and ammonical sodium bromate. Use of these chemicals can result in NH_3 concentrations of 700 - 5200 mg/l in the waste stream.[9] Analysis of wash water from an air preheater downstream of an SCR system indicated an average NH_3 concentration of 8 mg/l. (As a maximum, the NH_3 concentrations in air preheater wash water should be less than 100 mg/l.) These concentrations are less than those expected in typical metal cleaning wastes; as a result, the most significant impact of NH_3 in the air preheater wash water will be to increase the volume of metal cleaning waste water which must be treated.

Thermodynamic and Kinetic Analyses of NH_3-SO_3 Reactions

One objective of this study was to quantify the factors which influence the formation of $(NH_4)_2SO_4$/NH_4HSO_4 deposits. To achieve this objective, two types of analyses were conducted: (1) the thermodynamics of NH_3 reactions were evaluated to identify which reactions can occur in the preheater; and (2) a kinetic analysis was conducted to identify the factors which control the rate of $(NH_4)_2SO_4$/NH_4HSO_4 formation in the preheater.

Thermodynamics

The formation of both $(NH_4)_2SO_4$ and NH_4HSO_4 are temperature dependent reactions which proceed as a gas containing NH_3, SO_3, and H_2O is cooled. The temperature at which these reactions begin to occur will depend on the concentrations of reactants in the gas phase and on the product formed.

To quantify the relationship between reactant concentrations, products formed, and temperature, a thermodynamic analysis of the $(NH_4)_2SO_4$ and

NH_4HSO_4 formation reactions was conducted. This analysis employed thermodymanic principles to estimate the equilibrium concentrations of both reactants and products. The results of the analysis do not imply that the reactions which can occur will proceed at a rapid or even measurable rate. They do, however, identify reactions which will not proceed under certain circumstances.

The only significant NH_3 reactions which can occur in an air preheater are those which form $(NH_4)_2SO_4$ and NH_4HSO_4. In addition, H_2SO_4 can form from the reaction of SO_3 and H_2O. The thermodynamic analysis conducted as part of this study considered only these reactions.

Some typical results of the thermodynamic analysis are present in Figure 4 which shows the fractional extent of reaction (E) as a function of temperature for an initial SO_3 concentration of 10 ppm and various initial NH_3 concentrations. Fractional extent of reaction is defined here as the fraction of the stoichiometrically limiting species that can react for a given temperature and inlet NH_3/SO_3 concentrations as shown in Table 2.

A major result of the thermodynamic analysis is that $(NH_4)_2SO_4$ is the principal product at equilibrium for all the cases examined. This can be seen in Figure 4 which shows initial $(NH_4)_2SO_4$ formation temperatures that are 20 - 40°C higher than the NH_4HSO_4 formation temperatures. The reason for this is that, for a given temperature, the change in free energy for $(NH_4)_2SO_4$ formation is greater than the change in free energy for NH_4HSO_4 formation.

Another result of the thermodynamic analysis is that both $(NH_4)_2SO_4$ and NH_4HSO_4 form in a narrow temperature range. The temperature drop required to permit 90 percent reaction of NH_3 and SO_3 is approximately 30°C and approximately 20°C for 80 percent reaction. This is significant in terms of air preheater operation. It means that most deposition could be limited to a small region of the preheater.

Kinetics

The results of the thermodynamic analysis identify what reactions are possible at a given temperature, but they do not provide any information on the rate at which the reactions occur. Rate data can only be obtained by experimentation and subsequent analysis of the experimental results. As part of this study, Jumpei Ando conducted laboratory experiments on NH_3-SO_3 reactions and supplied the results of these experiments to Radian. A kinetic analysis of Ando's experimental results was conducted which identified possible rate limiting steps in the formation of ammonium sulfates in a heat exchanger. A model of $(NH_4)_2SO_4$/NH_4HSO_4 formation and deposition was then developed and applied to Ando's experiments.

The three phenomena which can limit the rate of $(NH_4)_2SO_4$ and/or NH_4HSO_4 formation in a heat exchanger are:
- Chemical Reaction Rate.
- Heat Transfer Rate.
- Mass Transfer Rate.

The model developed as part of this study incorporated several assumptions. First, NH_4HSO_4 was assumed to be the only compound found in the heat

Table 1. *Discharge Limits for Metal Cleaning Wastes*

Stream Pollutant	Emission Limit for New Sources, mg/l	
	Maximum	*Average*
Total Suspended Solids	*100*	*30*
Oil and Grease	*20*	*15*
Copper (total)	*1*	*1*
Iron (total)	*1*	*1*

Table 2. *Fractional Extent of Reaction Defined as a Function of Reaction Product and NH_3/SO_3 Mole Ratio*

NH_3/SO_3 Ratio		E^a
Bisulfate Formation	*Sulfate Formation*	
>1	*>2*	$(Y^i_{SO_3} - Y^f_{SO_3})/(Y^i_{SO_3})$
<1	*<2*	$(Y^i_{NH_3} - Y^f_{NH_3})/(Y^i_{NH_3})$

[a] *i = initial, f = final, and Y_2 = mole fraction of species a.*

exchanger. This assumption was made because analysis of deposits in Ando's experimental apparatus showed an NH_3/SO_3 mole ratio of 1.1 (i.e., the deposits were 90 percent NH_4HSO_4). Second, the rate of NH_4HSO_4 formation was assumed to be very rapid, such that the gas was at equilibrium with respect to NH_4HSO_4 formation in all areas of the heat exchanger. This means that NH_4HSO_4 can form as either a deposit on the heat exchanger surface or as an aerosol in the gas and the rate of aerosol/deposit formation is a function of the rate of heat and mass transfer in the heat exchanger.

A model based on these assumptions was applied to Ando's experimental heat exchanger resulting in a prediction of deposit and aerosol formation in the exchanger. Figure 5 presents typical model results and compares those results with some of Ando's experimental data. The figure shows the fractional amount of NH_3 and H_2SO_4 converted to NH_4HSO_4 as a function of distance in the experimental heat exchanger. The solid line in the figure is a smooth curve drawn through the data points from Ando's experimental results. The dashed lines represent the theoretical predictions from the model. The lower dashed line represents only the amount of NH_4HSO_4 predicted to form at the heat transfer surface. The upper dashed line represents the sum of the condensate and aerosol predicted to form.

The modeling results in Figure 5 appear similar to those obtained in the laboratory experiments, although the exact fate of the aerosols cannot be predicted. It does appear, however, that the assumptions made in developing the model are valid. At an initial NH_3/SO_3 mole ratio of 1.0, the principal reaction product appears to be NH_4HSO_4, and the reaction which forms this product is very rapid.

The fact that NH_4HSO_4 is the principal product formed is in apparent conflict with the thermodynamic predictions which indicate that $(NH_4)_2SO_4$ should be the only compound which forms, regardless of the initial NH_3/SO_3 stoichiometric ratio. Apparently, the reaction which forms $(NH_4)_2SO_4$ directly from gas phase reactants is slow relative to both the rate at which the gas is cooled from the sulfate to the bisulfate formation temperature and the rate of the reaction which produces NH_4HSO_4. As a consequence, the gas is cooled below both the $(NH_4)_2SO_4$ and
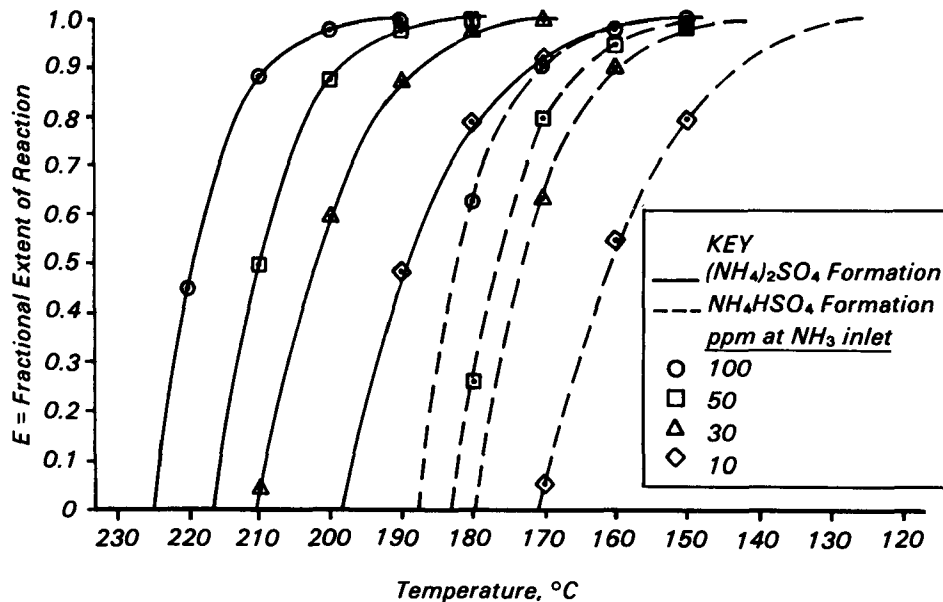

Figure 4. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 10 ppm SO_3 at inlet.
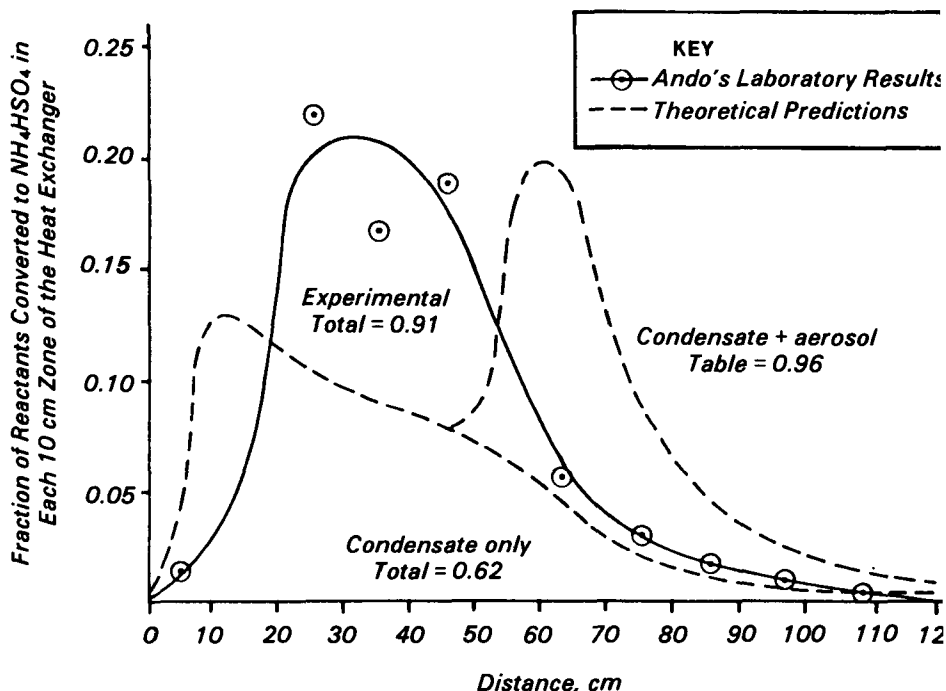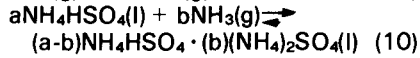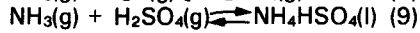

Figure 5. Predicted and actual NH_4HSO_4 formation for 600 Ncm/sec gas with 200 ppm each NH_3 and SO_3, and 160°C oil bath.

NH_4HSO_4 formation temperatures before appreciable quantities of $(NH_4)_2SO_4$ can form. At this point, the formation of NH_4HSO_4 predominates due to its more rapid reaction rate. This is not to imply that no $(NH_4)_2SO_4$ will

form in a preheater. On the contrary, significant quantities of $(NH_4)_2SO_4$ will form in the presence of excess NH_3.

In additional experiments using the laboratory-scale heat exchanger, Ando found that the composition of deposits

are related to the stoichiometric ratio of the reactants. Based on Ando's data and the results of the modeling work, it appears that the formation of ammonium sulfates proceeds via the reaction path shown in the following equations:

$$SO_3(g) + H_2O(g) \rightleftharpoons H_2SO_4(g) \quad (8)$$
$$NH_3(g) + H_2SO_4(g) \rightleftharpoons NH_4HSO_4(l) \quad (9)$$
$$aNH_4HSO_4(l) + bNH_3(g) \rightleftharpoons$$
$$(a-b)NH_4HSO_4 \cdot (b)(NH_4)_2SO_4(l) \quad (10)$$

Sulfuric acid vapor is the first product formed, and this reaction is essentially complete at the NH_4HSO_4 formation temperature. NH_3 then reacts with H_2SO_4 to form liquid NH_4HSO_4 which can further react with NH_3 as shown in Equation 10. The compound shown on the right side of Equation 10 represents a liquid solution of NH_4HSO_4 and $(NH_4)_2SO_4$.

In summary, the primary factors controlling NH_4HSO_4 and subsequent $(NH_4)_2SO_4$ formation are the concentrations of the gaseous reactants and the system temperatures. For given reactant concentrations, there is a specific temperature above which NH_4HSO_4 will not form. The phenomenon of NH_4HSO_4 deposition is more complex. The relative rates of heat and mass transfer must be considered to predict the amount of deposits.

Techniques for Minimizing Deposition of $(NH_4)_2SO_4/NH_4HSO_4$

Solutions to the $(NH_4)_2SO_4/NH_4HSO_4$ deposition problem should minimize or eliminate plugging and corrosion of the air preheater. This can be done in two ways: (1) modification of air preheater design and/or operation, and (2) modification of SCR system design and/or operation. The following discussion presents specific techniques for minimizing the problem.

Modification of Air Preheater Design/Operation

Four techniques identified for minimizing the impacts of deposit formation require modification of air preheater design or operation:

- Use of Available Air Preheater Design Options.
- Heat Cleaning of the Air Preheater.
- Flue Gas Recirculation for Selective Formation of $(NH_4)_2SO_4$.
- Increased Air Preheater Operating Temperature.

Each technique is discussed in detail below.

Use of Available Air Preheater Design Options

One way to limit the impact of $(NH_4)_2SO_4/NH_4HSO_4$ deposit formation is to use available options when specifying an air preheater design. Specifically, this includes:

- Both hot- and cold-end soot blowers.
- Increased soot blowing frequency.
- Increased soot blowing steam pressure.
- Provisions for in-service water washing of the preheater.
- Use of corrosion resistant material in both the intermediate and low temperature zones of the preheater.
- Use of combined intermediate and low temperature heat transfer elements.

Employing these options minimizes any impact associated with $(NH_4)_2SO_4/NH_4HSO_4$ deposition. Use of combined heat transfer elements, increased soot blowing intensity, and in-service washing should minimize plugging of the preheater, and the use of corrosion resistant material should permit reliable air preheater operation.

Each option will require some change in air preheater design or operation. Unfortunately, very little experience is available, and the effectiveness of the air preheater design options in limiting deposits is uncertain. However, EPDC has recently awarded a contract for two Ljunstrom heat exchangers to be installed downstream of an SCR system. These air preheaters incorporate most of the modifications recommended here; based on pilot-scale tests, EPDC expects them to operate without problems.[2]

Heat Cleaning of the Air Preheater

The fact that $(NH_4)_2SO_4/NH_4HSO_4$ deposits will decompose at elevated temperatures provides the basis for a second solution to the deposition problem.[10] This solution, termed "heat cleaning," requires that the operating temperature in the preheater be elevated to the point where $(NH_4)_2SO_4$ and NH_4HSO_4 will rapidly decompose (350 - 450°C). Periodic cleaning using this technique should help prevent deposit buildup.

Use of the heat cleaning technique has several drawbacks: (1) elevation of preheater temperatures will result in a temporary decrease in boiler efficiency; (2) the flue gas exiting the preheater

may need to be cooled to prevent damaging downstream equipment due to the high temperature of the gas (cooling the gas may also be required to recondense the $(NH_4)_2SO_4/NH_4HSO_4$ so these compounds can be collected in particulate control equipment); (3) if temperature gradients greater than those encountered during normal operation of the preheater occur during heat cleaning, differential expansion can damage the preheater; and (4) heat cleaning will effectively remove deposits of NH_4-Fe-SO_4 compounds and NH_4-fly ash-SO_4 compounds which can form in the preheater.

Use of heat cleaning to minimize air preheater deposits requires that several modifications be incorporated in the air preheater design. In particular, these modifications must include provisions for increasing the cold-end metal temperature. Examination of air preheater design characteristics indicates that the most promising technique of increasing the cold-end metal temperature involves eliminating the flow of air to the preheater while reducing the flue gas flow rate. This will result in raising the preheater temperature to the flue gas temperature with a minimum of problems. Since no air flows through the preheater during this period, differential expansion of the preheater wheel should be minimized. Also, since operation at a reduced flue gas flow will minimize the decline in boiler efficiency, it may not be necessary to cool the flue gas exiting the preheater with dilution air.

Note that this technique requires the boiler to have more than one preheater. Also, no data are available which indicate if heat cleaning will work or how effective it will be. This solution is based strictly on engineering judgement and requires experimental work to substantiate its feasibility. Technically, this solution is considered possible, but not proven.

Flue Gas Recirculation for Selective Formation of $(NH_4)_2SO_4$

The results of the thermodynamic analysis have identified several useful facts concerning the formation of ammonium sulfates. First, $(NH_4)_2SO_4$ forms at higher temperatures than NH_4HSO_4 and exists in pure form only as a solid. Second, at 20°C below the initial formation temperature, the $(NH_4)_2SO_4$ formation reaction can proceed to approximately 80 percent completion.

By modification of the air preheater design, it may be possible to exploit these facts to selectively form $(NH_4)_2SO_4$ and thereby minimize deposit formation.

One potential technique for selectively forming $(NH_4)_2SO_4$ employs flue gas recirculation from downstream of the air preheater to cool hot flue gas in a reaction chamber. Temperatures are controlled in the chamber so that $(NH_4)_2SO_4$ (but not NH_4HSO_4) is formed. The solid $(NH_4)_2SO_4$ should then pass through the preheater and be collected by particulate control equipment.

Two preheater designs can be used with flue gas recirculation: split and single. The split design divides a single air preheater into two preheaters in series, separated by a reaction chamber. The first air preheater is operated such that the cold-end metal temperature is maintained above the $(NH_4)_2SO_4$ formation temperature. Cooled flue gas is recirculated from downstream of the second preheater and injected into the reaction chamber. The recirculation rate is controlled to cool the flue gas in the reaction chamber below the formation temperature of $(NH_4)_2SO_4$ but not that of NH_4HSO_4. This should result in the formation of solid $(NH_4)_2SO_4$ only.

An alternative to the split air preheater design is a single air preheater in which flue gas is recirculated from the cold-end to a reaction chamber upstream of the hot-end. The recirculation rate is controlled to maintain the flue gas temperature entering the preheater below the formation temperature of $(NH_4)_2SO_4$ but above that of NH_4HSO_4. In principal, this technique is identical to use of a split air preheater. However, in practice, use of a single preheater would require recirculation of more flue gas and a larger preheater.

Flue gas recirculation was identified as a possible solution to the deposition problem, based strictly on the thermodynamic analysis of $(NH_4)_2SO_4/NH_4HSO_4$ formation. However, there are factors which make the feasibility of this solution uncertain. First, there are no data on the rate at which $(NH_4)_2SO_4$ forms from gas-phase reactants. All experimental data, including analysis of air preheater deposits, indicate that NH_4HSO_4 is the first product to form from gaseous reactants. The results of Radian's kinetic analysis confirms that the NH_4HSO_4 formation reaction occurs very rapidly, but the $(NH_4)_2SO_4$ formation rate could not be determined. Therefore, it may be impossible to selectively form $(NH_4)_2SO_4$ with a realistically sized reaction chamber residence time (i.e., 1 to 2 sec).

A second problem associated with flue gas recirculation is one of process control. Changes in fuel sulfur content or excess air to the boiler may change the SO_3 concentration, while changes in flue gas flowrate and NO_x concentration can change the concentration of NH_3 which is emitted from the reactor. If the air preheater is designed for one range of NH_3-SO_3 concentrations and a significant change in these concentrations occurs, it will be difficult to control the system to limit $(NH_4)_2SO_4$ formation to the reaction chamber and to prevent NH_4HSO_4 formation. The principal reason for this is that both NH_3 and SO_3 must be measured continuously to adjust the recirculation rate to the reaction chamber and thus control formation of $(NH_4)_2SO_4$. Unfortunately, both NH_3 and SO_3 are difficult to measure continuously.

The problems associated with use of flue gas recirculation represent significant technical obstacles. No data are available to indicate whether it is possible to selectively produce $(NH_4)_2SO_4$. In addition, the control problems associated with changing NH_3-SO_3 concentrations will be difficult to resolve. Therefore, the technical feasibility of using flue gas recirculation to prevent deposit formation is considered low.

Increased Air Preheater Operating Temperature

The most direct way to minimize the deposition of ammonium sulfates is to increase the air preheater operating temperature above that at which NH_4HSO_4 forms. This should minimize plugging and corrosion since any $(NH_4)_2SO_4$ and/or deposits which form, will be non-corrosive. These deposits will occur in the extreme cold-end of the preheater and should be easily removed by soot blowing.

Modification of the air preheater design to permit operation at a higher temperature should be relatively simple. The principal change required is a reduction in thermal efficiency of the preheater. Efficiency can be reduced by reducing the size of the preheater so the cold-end temperature is above that of NH_4HSO_4 formation.

The major impact of increasing the cold-end metal temperature will be to decrease boiler efficiency. In addition, there may be some impacts on downstream equipment and possibly an environmental impact due to gas-phase NH_3 and SO_3 emissions. For these reasons, it may be necessary to cool the flue gas exiting the preheater below the NH_4HSO_4 formation temperature.

Modification of SCR Design/Operation

A second approach to solving the $(NH_4)_2SO_4/NH_4HSO_4$ deposition problem is to modify the SCR system design and/or operation. The intent of modifying the SCR system is to reduce the NH_3 emissions from the reactor, thereby reducing the formation of ammonium sulfates in the preheater. There is basically one way to modify the SCR system so that the NH_3 emissions are reduced. Additional catalyst can be used and the NH_3 injection rate can be lowered while maintaining the desired NO_x removal level, thus reducing the NH_3 emissions.

The design of an SCR system is influenced by a trade-off between the quantity of catalyst in the reactor, the NH_3 injection rate, and the NO_x removal efficiency of the system. By increasing the quantity of catalyst and simultaneously reducing the NH_3 injection rate, the NH_3 emissions can be reduced while maintaining a constant NO_x removal efficiency. This relationship is quantified in Table 3. As shown, NH_3 emissions for the base case are 30 ppm. The use of about 30 percent additional catalyst (Case 2) can reduce NH_3 emissions to about 10 ppm while 70 percent more catalyst (Case 3) should effectively eliminate NH_3 emissions.

The most significant impact of increasing the amount of catalyst in the reactor will be to increase the capital investment and operating costs for the SCR system.

Table 3. *Effect of Increased Catalyst on NH₃ Emissions*[3, 11]

Case	Base	1	2	3
Relative Catalyst Amount	1.0	1.10	1.31	1.71
NH_3/NO_x for 90% Removal	1.0	0.98	0.95	0.92
NH_3 Emissions, ppm	30	20	10	0

Estimated Costs for Proposed Solutions to the Deposition Problem

Cost estimates were prepared to determine the incremental capital and first year annualized costs for each solution identified by this study. The basis for these estimates is defined in Table 4. Incremental costs were determined for each modification required to implement a proposed solution using the flowrates, temperatures, and other characteristics of the system defined in Table 4. The following discussion presents the results of the cost estimates, along with a specific definition of the modifications included in making those estimates.

Air Preheater Design Option Costs

Table 5 compares design options added to the preheater to minimize deposit formation with an unmodified preheater design. Table 6 contains cost estimates for the preheater design options. As shown, soot blowing costs will increase significantly due to an increase in both the number of soot blowers and the soot blowing frequency. Also, material costs will increase significantly due to the corrosion resistant material used in the intermediate temperature zone of the preheater.

Air Preheater Heat Cleaning Costs

Table 7 gives estimated incremental capital and first year annualized costs for air preheater heat cleaning. The costs associated directly with heat cleaning include fuel costs which result from raising the flue gas exit temperature from 150 to 350°C for 30 minutes per day at 10 percent of the maximum flue gas flow rate.

Flue Gas Recirculation Costs

Table 8 gives estimated costs for the two flue gas recirculation options defined in this study. The capital costs shown include the incremental costs for an additional or larger air preheater, recirculation fans, ducts for flue gas recirculation, and a reaction chamber. Included in the annualized cost estimates is a heat credit which results from assuming that flue gas temperature at the air preheater exit can be reduced from 150 to 115°C due to neutralization of H_2SO_4 in the gas.

Table 4. Basis for Estimating Incremental Costs of Proposed Solution

Parameter	Base Value
Boiler Characteristics	
• Size	500 MWe
• Thermal Efficiency	88%
• Number of Air Preheaters	2
• Flue Gas Flowrate	620 kg/sec (82,000 lb/min)
• Heat Rate	9.5 MJ/kWh (9000 Btu/kWh)
• Operating Factor	7000 hrs/yr
Flue Gas Characteristics	
• Reactor Inlet	
—NO_x concentration	350 ppm
—NH_3 concentration	350 ppm
—SO_3 concentration	10 ppm
—temperature	350°C
• Reactor Outlet	
—NO_x concentration	35 ppm
—NH_3 concentration	30 ppm
—SO_3 concentration	10 ppm
• Air Preheater Outlet	
—NO_x concentration	35 ppm
—NH_3 concentration	20 ppm
—SO_3 concentration	0 ppm
—NH_4HSO_4 concentration	10 ppm equivalent
—temperature	150°C
SCR Characteristics	
• Relative Quantity of Catalyst	1.0
• NO_x Removal Efficiency	90%
• NH_3/NO_x Mole Ratio	1.0
Air Preheater Characteristics	
• Type/Size	Ljungstrom Tri-Sector/Size 31
• Number of Soot Blowers	1/ air preheater (cold-end)
• Soot Blowing Frequency	3/day
• Soot Blowing Steam Pressure	1.48 MPa (200 psig)
Cost Characteristics	
• Year	1979 Capital/1980 annualized[a]
• Fuel Cost	$2.37/GJ
• Air Preheater Capital Cost	$2,600,000
• Type of Installation	New
• Capital Recovery Factor	14.6% of capital investment

[a]Annualized costs include annual operating and maintenance costs (including fuel) plus capital-related charges such as depreciation, return-on-investment, and interest-on-debt.

Table 5. A Comparison of Modified Preheater with Basic Preheater Design Specifications

Specification	Basic Design	Modified Design
Number of Soot Blowers	1 - Cold end only	3 Cold end 3 Hot end
Soot Blowing Frequency	3/day	6/day
Soot Blowing Steam Pressure	1.48 MPa	1.82 MPa
Materials of Construction		
- intermediate temp zone	Light gauge carbon steel	Combined intermediate and low temperature zones
- low temp zone	Heavy gauge carbon steel	304 stainless steel

Increased Air Preheater Operating Temperature Costs

Table 9 shows incremental first year annualized costs for increasing the preheater operating temperature above the NH_4HSO_4 and $(NH_4)_2SO_4$ formation temperatures. For this study, no change in capital costs was considered since no additional capital expenditures are required. The annualized costs given in Table 9 are based on increased fuel costs which result from raising the flue gas exit temperature to 230°C and 250°C for prevention of NH_4HSO_4 and $(NH_4)_2SO_4$ formation, respectively.

Increased Catalyst Costs

Table 10 gives the incremental capital and annualized costs incurred to reduce NH_3 emissions to 10 ppm by increasing the quantity of catalyst in the reactor. The estimates of Table 10 include incremental capital charges for the initial catalyst charge, higher reactor and annual costs for catalyst replacement, and a credit for reduced NH_3 ammonia consumption.

Conclusions

The major conclusions of this study are:

* NH_3 leakage from SCR reactors can be a problem for an air preheater downstream of the reactor. However, operating experience indicates that NH_3 concentrations below 10 ppm at the air preheater entrance do not result in serious deposition problems. This is probably due to the fact that at low NH_3 concentrations, ammonium sulfates form in the cold end of the preheater where soot blowing equipment effectively removes deposits.
* The effects of the deposition problem are limited to plugging of the preheater and corrosion of preheater materials in the intermediate temperature zone. The ability of the preheater to transfer heat should not be significantly impaired by deposit buildup. In addition, normal corrosion in the extreme cold end of the preheater will be reduced due to neutralization of SO_3-H_2SO_4 by NH_3.
* No significant environmental problems will result from washing deposits from the air preheater. The NH_3 levels in the preheater wash water will be lower than those typically encountered in power plant metal cleaning wastes. A slight increase in waste treatment costs may result due to the increased volume of wash water. The magnitude of this cost increase is site specific and depends on the method of waste water treatment employed.
* The problems associated with deposition of $(NH_4)_2SO_4/NH_4HSO_4$ can be minimized or eliminated by several techniques. A relative technical and economic ranking of these techniques is given in Table 11. As shown, solutions with the lower technical feasibility have the lower costs, while the solutions with the higher technical feasibility incur higher costs.
* Based on the results in Table 11, it appears that use of available air preheater design options is the optimum solution to the deposition problem both technically and economically. However, the solutions with low technical feasibility could result in lower annualized costs and thus merit further investigation.

Table 6. Estimated Capital and First Year Annualized Costs for Air Preheater Design Options

Option	Incremental Capital Costs, $1000's	Incremental Annualized Costs, $1000's
Soot Blowing Modifications	158	233
In-Service Washing	0	18
Corrosion Resistant Material	1376	201
TOTAL	1534	452

Table 7. Estimated Capital and First Year Annualized Costs for Air Preheater Heat Cleaning

Option	Incremental Capital Costs, $1000's	Incremental Annualized Costs, $1000's
Heat Cleaning	370	70
Corrosion Resistant Material	1376	201
TOTAL	1746	271

Table 8. Estimated Incremental Capital and First Year Annualized Costs for Flue Gas Recirculation

Method	Incremental Capital Costs, $1000's	Incremental Annualized Costs, $1000's
Single Preheater	9690	857
Split Preheater	6223	(198)

Table 9. Incremental First Year Annualized Costs for Increasing Air Preheater Operating Temperature

Option	Cold End Temperature °C	Annualized Costs $1000's
Prevent NH_4HSO_4 Formation	230°C	3098
Prevent $(NH_4)_2SO_4$ Formation	250°C	4270

Table 10. Estimated Incremental Capital and First Year Annualized Costs for an Increased Catalyst Charge

Catalyst Life years	Capital Costs $1000's	Annualized Costs $1000's
1	6054	3640
2	6054	2248

• Table 12 gives the annualized costs for various solutions to the deposition problem as a percentage of the annual revenue requirements for SCR. As shown the cost impact of the solutions ranges from a 1.6 percent reduction to a 30 percent increase in annualized costs.

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Table 11. Technical and Economic Ranking of Proposed Solutions to the $(NH_4)_2SO_4/NH_4HSO_4$ Deposition Problem

Solution	Relative Technical Feasibility[a]	Estimated Incremental First Year Annualized Costs 1000's
Air Preheater Design Options	Intermediate	452
Heat Cleaning	Low	271
Flue Gas Recirculation		
- Single Preheater	Low	857
- Split Preheater	Low	(198)
Increased Cold-End Metal Temperature	High	3,098
Increased Catalyst/Decreased NH_3/NO_x	Intermediate	3,668[b,c]

[a]These are somewhat subjective and based on engineering judgment.
[b]This cost is based on reducing NH_3 emissions to approximately 10 ppm.
[c]Assumes a 1-year catalyst life (current vendor guarantee for coal-fired applications).

Table 12. Estimated Increase in SCR Annualized Costs for Proposed Solutions to the $(NH_4)_2SO_4/NH_4HSO_4$ Deposition Problem

Solution	Increase (Decrease) in SCR Costs, %
Air Preheater Design Options	3.7
Heat Cleaning	2.2
Flue Gas Recirculation	
- Single Preheater	7.0
- Split Preheater	(1.6)
Increased Cold-End Metal Temperature	25.4
Increased Catalyst/Decreased NH_3/NO_x	30.0

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