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FLUE GAS CONDITIONING

by

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| agents and user experience. Many existing | chemicals have been use | d as conditioning | | |
| agents in power plants or have been studied | I in the laboratory as pot | ential agents. | | |
| The particle collection efficiency of an elec | ctrostatic precipitator (E | SP) for coal-fired | | |
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| FSP to improve the collection efficiency of | ESPs Conditioning is up | sually used to | | |
| ungrade existing ESPs | | | | |
| upgrade existing Lors, | | | | |
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ABSTRACT

The particle collection efficiency of an electrostatic precipitator (ESP) for coal-fired power plant flue gas cleaning depends on the electrical properties of the fly ash, among other things. Flue gas conditioning refers to the addition of chemicals to the flue gas for modification of fly ash properties and/or electrical conditions in the ESP and thus improve the collection efficiency of ESP's. It is usually used for upgrading existing ESP's.

Many existing chemicals have been used as conditioning agents in power plants or have been studied in the laboratory as a potential agent. This report presents the results of a survey of available agents and user experience.

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Section 1 SUMMARY AND CONCLUSIONS

FLUE GAS CONDITIONING

Flue gas conditioning refers to the addition of chemicals to the flue gas in a coal-fired power plant for modification of fly ash properties and/or electrical conditions in the electrostatic precipitator (ESP) and thus improve the collection efficiency of ESP's. It is usually used to retrofit existing ESP's whose performance has deteriorated, or which are operating below design efficiency.

The collection of fly ash in an ESP involves the precipitation of the ash followed by its successful removal: first from the collection plates and then the hoppers. For a precipitator of given size and operating under fixed conditions, the collection efficiency of the ESP is affected by the following parameters:

- the electric field strength and ion density in the precipitation zone,
- 2. the adhesive and cohesive properties of the fly ash, and
- 3. the average particle size and size distribution.

A conditioning agent may operate by affecting some or all of these factors. The ash resistivity is important because it can affect both "1" and "2".

CONDITIONING MECHANISMS

A conditioning agent may influence the ESP collection efficiency through one or more of the following mechanisms:

- Adsorbs on surface of fly ash and reduces surface resistivity.
- Adsorbs on fly ash and changes the adhesion and cohesion properties of ash.
- Increase ultrafine particle concentrations for space charge enhancement.
- 4. Increase electrical breakdown strength of flue gas.
- 5. Increase the mean particle size.

6. Change the acid dew point in the flue gas.

The effects of these mechanisms on ESP performance are described in Table 1.

FLUE GAS CONDITIONING AGENTS

Many chemicals have been used as conditioning agents in power plants or have been studied in the laboratory as a potential conditioning agent. Table 2 shows a list of these chemicals and their principal conditioning mechanisms.

Sulfur Trioxide

Sulfur trioxide (which readily becomes sulfuric acid when water is present) is the most widely used conditioning agent in the U.S. It is a natural component of flue gas from fossil fuel combustion. It is hygroscopic and has a very low volatility so it condenses easily. When adsorbed or condensed on the ash, it forms a layer of conductive solution on the ash surface to reduce the ash resistivity.

For conditioning, SO₁ is produced by one of the following four processes:

- 1. vaporization of a sulfuric acid solution,
- 2. vaporization of liquid sulfur trioxide,
- vaporization of liquid sulfur dioxide and oxidization to sulfur trioxide over a vanadium pentoxide catalyst.
- 4. burning liquid sulfur in air to produce sulfur dioxide and then oxidize to SO₂.

Ammonia

Ammonia is a vapor at room conditions and has a critical temperature of 132°C. Above this temperature ammonia exists as a single phase and cannot boil or condense. Therefore, condensation on the fly ash would not be expected to occur with ammonia above 132°C, although adsorption could take place.

Because of the high volatility of ammonia, it is injected in the vapor form under its own vapor pressure. In Australia, ammonia is also injected in solution form.

| Effect of Conditioning Agent | Electrical Result | Mechanical Result | Effect on Efficiency | Comments |
|--|---|---|-------------------------|--|
| Adsorbs on surface of fly ash and reduces surface resistivity - | OIncreases the magnitude of the precipitation field oReduces the voltage drop in the dust layer oDelays the onset of back corona oIncreases the sparkover voltage | | •• | Useful for high resistivity dusts: O Increases charging and precipitation field strength O Reduces the electrical adhesion on the wall and thus improves the effectiveness of rapping |
| | OREGUCES the electrical ad- hesion effect on the wall | | + or - | Beneficial for high resistivity dusts. If used with low or medium resistivity dusts, further lowering of adhesion forces could lead to reentrainment losses. |
| Adsorbs on fly ash and changes cohesiveness or "stickiness" | | Aids agglomeration and increases mean particle size | • | Size enhancement may occur indepen- dently of resistivity change and thus improve migration velocity. OLarger size fraction also aids removal by rapping |
| | | Dust layer on wall becomes more cohesive | + | o Cohesive dust layer tends to shear off collecting plate with less re-entrainment losses |
| | | Dust layer has stronger adhesion to wall | + or - | Stronger adhesion is an advantage for low resistivity dusts Could be a disadvantage for high resistivity dusts |
| Increases particle concentration due to presence of "fines" (i.e., particulate reaction products) | Reduces ion density (and thus current) due to space charge suppression | | + or - | The current reduction could reduce charging effectiveness On the other hand, the lower current density will alleviate field re- duction problems caused by the voltage drop through a high resistance dust layer |
| | o Increases collection field strength due to space charge enhancement | | + | Space charge increases the field strength near the collecting electrode |
| | OIncreames sparkover voltage | | + | A slight increase in sparkover voltage usually results from increased space charge |

TABLE 1. POSSIBLE MECHANISMS WHEREBY A CONDITIONING AGENT MAY AFFECT PRECIPITABILITY (CASTLE, 1980)

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| TABLE] | l cont: | inued |
|---------|---------|-------|
|---------|---------|-------|

| Effect of Conditioning Agent | Electrical Result | Mechanical Result | Effect on Efficiency | Comment |
|---|--|-------------------|-------------------------|---|
| Increases electrical breakdown strength of flue gas | Increases the magnitude of the precipitator field: oIncreases sparkover voltage oDelays onset of back corona | | • • | The breakdown characteristics of flue gases are very sensitive to minor concentrations of electro-negative species and to surface conditions of the dust layer. This can be independent of fly ash resistivity. |
| Neutralization of acid in flue gas | Decreases acid dev- point. This reduces surface "tracking" on high voltage insulators allowing higher voltages to be applied | | * * | With some high sulfur coals, the sulfuric acid concentration in the flue gas is so high that the acid dew point may be above the flue gas temperature. This may result in acid condensation on support insulators. |

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 + + Indicates strong tendency to increase efficiency.
 + Indicates tendency to increase efficiency.
 - Indicates tendency to decrease efficiency. KEY

Ref.: Castle, G. S. P. "Mechanisms Involved in Fly Ash Precipitation in the Presence of Conditioning Agents -A Review." IEEE Trans. Ind. Appl. <u>IA-16</u>: 297-302 (1980).

TABLE 2. FLUE GAS CONDITIONING AGENTS AND CONDITIONING MECHANISMS

Conditioning Agent

Conditioning Mechanisms

SO3, (H2SO4)

NH 3

Resistivity modification

Adhesion and cohesion improvement Space charge enhancement

Ammonium Compounds (SO₂OH)NH₂ (sulfamic acid) (NH₄)₂SO₄ NH₄HSO₄ (NH₂)₂CO (NH₄)₂HPO₄ Space charge enhancement Resistivity modification

Organic Amines (CH₃CH₂)₃N (Triethylamine) (CH₃)₃N (Trimethylamine) (C₆H₁₁)NH₃ (Cyclohexylamine)

Resistivity modification

Alkali Compounds Na₂SO₄ Na₂CO₃

Proprietary Compounds Apollo LPA-30 Apollo LPA-40 Apollo LPA-50 Koppers "K"

Resistivity modification

Resistivity modification Space charge enhancement

Ammonium Compounds

Conditioning with ammonium compounds offers a more convenient method of injecting ammonia. The commonly used ammonium compounds are sulfamic acid, ammonium sulfate, and ammonium bisulfate. If injected upstream of the air pre-heater, these compounds could decompose to ammonia and sulfuric acid and may provide a combination of the effects of ammonia and sulfuric acid conditioning.

Organic Amines

Organic amines have been studied in the laboratory and pilot scale ESP's as possible flue gas conditioning agents. Currently, there are no industrial users. Of all the amines, triethylamine has received the most attention. It is an organic nitrogen compound and is highly soluble in water. It behaves similar to ammonia, but is a substantially stronger base. The melting and boiling points of triethylamine are -115°C and 90°C. It primarily decomposes to ammonia, hydrogen cyanide, nitrogen dioxide, and nitric oxide at temperatures above 340°C (650°F).

Dry Alkali

When the SO; concentration is low or when the temperature is above 200°C, the ash resistivity is indirectly related to the alkali metal content in the ash and reduction of ash resistivity by increasing the alkali metal concentration has been tried. Of the many alkali metal salts, sodium salts are the most commonly used conditioning agents because of their availability and relatively low cost. The widely used sodium compounds are sodium carbonate and sodium sulfate. Sodium chloride has been tried in the laboratory and found to be effective. However, it is not used because it can lead to corrosion of metal equipment.

The mechanism for sodium conditioning depends on how the sodium is applied. If a sodium compound is injected into the boiler along with coal, it will decompose and the sodium is bound in the ash. The sodium will increase the conductivity and lower the ash resistivity the same way as natural sodium.

If the sodium compound is co-precipitated with the ash, the compound trapped in the space between the particles on the dust layer offers an additional conductive path for charge dissipation.

Proprietary Formulations

Most of the proprietary chemicals are ammonium compounds with minor additives, such as surface active agents. Therefore, these chemicals perform similarly to ammonium compounds.

Miscellaneous Compounds

Several metal oxides, such as iron oxide and vanadium oxide, have been investigated as possible conditioning agents (Kanowski and Coughlin, 1977). Iron and vanadium oxides are claimed to catalyze the reaction of SO₂ to SO₃ and thus increase the quantity of SO, present in the flue gas. This claim has not been substantiated in the literature.

RESULTS

Table 3 shows a list of past and present flue gas conditioning users in the U.S.A. Summaries of user experiences are presented in the following sections.

Sulfur Trioxide

SO; conditioning is limited to cold side ESP's. The most common injection location is between the air preheater and the electrostatic precipitator inlet. The temperature at the point of injection and in the precipitator should be above the sulfuric acid dew point of the gas after addition.

The dosage for SO; injection normally is in the range of 5 to 30 ppmv; but can be as high as 70 ppmv. The required dosage will depend on the composition of the ash surface, i.e., whether it is acidic, neutral, or basic. If the ash has a large amount of alkaline compounds, a higher dosage of SO; is needed because

| Company Name | Plant_Name | Boiler Number | FGC_Licensor | EGC_Agent |
|--|----------------|-----------------|-------------------|-----------------|
| Alabama Power Co. | Barry | 4 | Wahlco | Sulfur trioxide |
| AEPSCO Appalachian Power | Cabin Creek | | | |
| AEPSCO Appalachian Power | Kanawha River | | | |
| AEPSCO Columbus & Southern Ohio Electric | Conesville | 4 | | |
| Arizona Public Service Co. | Four Corners | 4 | Apollo | LPA-445 |
| Baltimore Gas & Electric | H. A. Wagner | 3 | Apollo | |
| Central Illinois Light | Duck Creek | | Apollo | |
| Central Illinois Light | E. D. Edwards | 1,2,3 | Wahlco | Sulfur trioxide |
| Central Illinois Light | R. S. Wallace | 7,8,9,10 | Wahlco | Sulfur trioxide |
| Cincinnati Gas & Electric Co. | W. C. Beckjord | 1,2,4 | Wahlco | Sulfur trioxide |
| City of Colorado Springs DPU | Nartin Drake | 1,5 | Research-Cottrell | Sulfur trioxide |
| Cleveland Electric Illuminating Co. | Ashtabula | 5 | Wahlco | Sulfur trioxide |
| Cleveland Electric Illuminating Co. | Avon Lake | 9 | Wahlco | Sulfur trioxide |
| Cleveland Electric Illuminating Co. | Eastlake | 5 | Wahlco | Sulfur trioxide |
| Cleveland Electric Illuminating Co. | Lake Shore | 18 | Wahlco | Sulfur trioxide |
| Colorado-Ute Electric Assoc. | Hayden | 1,2 | Apollo | |
| Commonwealth Edison | Crawford | 7,8 | Wahlco | Sulfur trioxide |
| Commonwealth Edison | Fisk | 19 | Wahlco | Sulfur trioxide |
| Commonwealth Edison | Joliet | 3,4,5,6 | Wahlco | Sulfur trioxide |
| Commonwealth Edison | Joliet | 71,72,81,82 | | |
| Commonwealth Edison | Powerton | 51,52 | Wahlco | Sulfur trioxide |
| Commonwealth Edison | Waukegan | 15,16,17,8 | Wahlco | Sulfur trioxide |
| Commonwealth Edison | Will County | 4 | Wahlco | Sulfur trioxide |
| Commonwealth Edison/Indiana | State Line | 1-1,1-2,1-3 | Wahlco | Sulfur trioxide |
| Commonwealth Edison/Indiana | State Line | 1-4,1-5,1-6 | | |
| Commonwealth Edison/Indiana | State Line | 2-1,2-2,2-3,3,4 | | |
| Consumers Power Co. | B. C. Cobb | 1,2,3,4,5 | Wahlco | Sulfur trioxide |
| Consumers Power Co. | J. C. Weadock | 7,8 | Wahlco | Sulfur trioxide |
| Detroit Edison | Conners Creek | 15,16 | Wahlco | Sulfur trioxide |
| Detroit Edison | Harbor Beach | 1 | Wahlco | Sulfur trioxide |
| Detroit Edison | Monroe | 1,2 | Wahlco | Sulfur trioxide |

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TABLE 3. LIST OF PAST AND PRESENT FLUE GAS CONDITIONING USERS

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TABLE 3. Continued

| Company_Name | Plant Name | Boiler Number | FGC Licensor | FGC Agent |
|--|-----------------------|---------------|-------------------|---------------------------------------|
| Detroit Edison | Pennsalt | | UOP | Sulfur trioxide |
| Detroit Edison | Port Muron | 5 | Wahlco | Sulfur trioxide |
| Detroit Edison | Trenton Channel | 7,8,9A | Wahlco | Sulfur trioxide |
| Duke Pover | Belevs Creek | 1,2 | Research-Cottreli | Sulfur trioxide |
| Duke Pover | Marshall | | | |
| East Kentucky Rural Electric Power Coop. | W. C. Dale | 3,4 | Wahlco | Sulfur trioxide |
| Florida Power | Crystal River | 2 | Apollo, Nalco | · · · · · · · · · · · · · · · · · · · |
| Georgia Power | Harllee Branch | 3,4 | Apolio | |
| Gulf Power Co. | Scholz | | • | |
| Iova Public Service Co. | G. W. Neal | 2,4 | Wahlco | Sulfur Trioxide |
| Lansing Board of Water & Electric Light | Erickson | 1 | Wahlco | Sulfur trioxide |
| Nontana Power Co. | J. E. Corette | 1 | Apollo | LPA-40 |
| New England Power Co. | Salem Harbour | | Nalco | |
| New England Power Co. | Brayton Point | | Nalco | |
| New Jersey Gas 6 Electric | Nercer | | Apollo | LPA-40 |
| New York State Electric & Gas | Goudey | 11,12 | Wahlco | Sulfur trioxide |
| New York State Electric & Gas | Gceenidge | 4,5,6 | Wahlco | Sulfur trioxide |
| Northern Indiana Public Service Co. | D. H. Mitchell | 4,5,6,11 | Wahlco | Sulfur trioxide |
| Northern Indiana Public Service Co. | D. H. Hitchell | | Apollo | |
| Ohio Edison Co. | Edgewater | | Dusco | |
| Ohio Edison Co. | Gorge | | Dusco | |
| Ohio Edison Co. | W. H. Sammis | 1,2,3,4,5,6,7 | Wahico | Sulfur trioxide |
| Ohio Edison Co. | W. H. Sammis | | Apollo | |
| Pacific Power & Light | Bridger | | | 'Ammonia |
| Pacific Power & Light | Centralia | 1,2 | | |
| Pennsylvania Electric Co. | Front Street | 9,10 | Wahlco | Sulfur trioxide |
| Pennsylvania Electric Co. | Keystone | 1,2 | | |
| Pennsylvania Power & Light Co. | Brunner Island | 1,3 | Wahlco | Sulfur trioxide |
| Pennsylvania Power & Light Co. | Montour | 1,2 | Wahlco | Sulfur trioxide |
| Pennsylvania Power & Light Co. | Montour | | Apollo | LPA-402A |
| Pennsylvania Power & Light Co. | Sunbury | 3,4 | Wahlco | Sulfur trioxide |
| Public Service Co. of Colorado | Acapahoe | 1,2,3,4 | Wahlco | Sulfur trioxide |

TABLE 3. Continued

| Company_Name | <u>Plant Name</u> | Boiler Number | FGC Licensor | FGC Agent |
|---|-------------------|---------------|----------------|-----------------|
| Public Service Co. of Colorado | Cameo | 2 | | |
| Public Service Co. of Colorado | Cherokee | 1,2,3,4 | Lodge-Cottrell | Sulfur trioxide |
| Public Service Co. of Colorado | Comanche | 1,2 | | |
| Public Service Co. of Colorado | Valmont | 5 | Nalco | |
| Public Service Electric & Gas, New Jersey | Rudson | | Apollo | , |
| Public Service Electric & Gas, New Jersey | Mercer | | Apollo | LPA-40 |
| Salt River Project | Hayden | 2 | | |
| South Carolina Public Service Authority | Jefferies | 3,4 | Apollo | LPA-40 |
| Tampa Electric Co. | Big Bend | | | |
| Tampa Electric Co. | F. J. Gannon | 5,6 | Apollo | LPA-40 |
| Tennessee Valley Authority | Bull Run | 1 | | Ammonia |
| Tennessee Valley Authority | Gallatin | 4 | | Ammonia |
| Tennessee Valley Authority | Kingston | 5 | | |
| Tennessee Valley Authority | Shavnee | 10 | | |
| Tennessee Valley Authority | Widows Creek "B" | 7,8 | | Ammonia |
| TUGCO Dallas Power and Light | Big Brown | | Apollo | |
| TUGCO Dallas Power and Light | Monticello | 1,2 | Apollo | |
| Toledo Edison | Bayshore | | Nalco | · |
| UGI Corp. Luzerne Electric | Hunlock Creek | | UOP | Sulfur trioxide |
| Upper Peningula Generating Corp. | Presque Isle | 1,2,3,4,5,6 | Apollo | Sulfur trioxide |
| Upper Peningula Generating Corp. | Presque Isle | 1,2,3,4,5,6 | Wahico | Sulfur trioxide |
| Utah Power and Light | Naughton | 3 | Wahlco | Sulfur trioxide |
| Virginia Electric & Power | Yorktown | | Apollo | |
| Wisconsin Electric Power Co. | Pleasant Prairie | 1,2 | Wahlco | Sulfur trioxide |
| Wisconsin Power & Light | Columbia | 1 | | |

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the alkaline compound will react with, or neutralize, the condensed sulfuric acid.

SO₃ conditioning is effective in reducing ash resistivity and improving the ESP performance in those cases where particle resistivity is the limiting factor in ESP performance. In general, an addition rate of 20 ppmv can lower the resistivity by two orders of magnitude (from about 10° to 10¹⁰ Ohm-m to 10⁷ to 10° Ohm-m).

There are cases where SO, conditioning has not been effective. The reason could be among the following:

- 1. The conditioner supply malfunctioned.
- The ESP performance is limited by other phenomena besides ash resistivity.
- 3. The ash resistivity may already be satisfactory.
- 4. The temperature may be so low that acid condensation occurs at the injection point before the SO₃ is mixed with the flue gas.
- 5. The temperature is much higher than the acid dew point.

Even though SO, conditioning can improve the particle collection efficiency of the ESP, it can increase the emissions of sulfuric acid mist and particulate sulfate compounds. The emission rate of added SO, is higher for acidic ashes and high gas temperatures.

Due to increased particle collection by the ESP, the plume opacity is usually lower with conditioning. However, an "acid plume" could be formed if the sulfur trioxide dosage and gas temperature are too high.

Operating Problems

Interviews with several users of sulfur trioxide conditioning revealed the following categories of operating difficulties:

- 1. Corrosion of injection lines.
- 2. Deactivation of catalysts in the SO₂ to SO₃ converter.
- 3. Over conditioning (resistivity lowered too much).

Economics

The estimated capital and operating costs of a sulfur trioxide flue gas conditioning installation as of December, 1982 are \$5.15/kW and 0.105 mills/kWh, respectively.

Ammonia

Ammonia is injected either before or after the air preheater in vapor or liquid form. Most of the users inject it downstream of the air preheater to avoid plugging of the preheater with deposits of ammonia reaction products.

The ammonia injection dosage is about 15 to 20 ppmv. In most situations, ammonia can improve the ESP performance. However, the way in which ammonia affects the performance of ESP's is not completely understood. The effectiveness of ammonia appears to depend mainly upon the initial ash resistivity, flue gas composition, and temperature.

The ability of ammonia to alter resistivity is not clear. Ammonia conditioned resistivities can be less than, the same as, or greater than the unconditioned values. The temperature of the precipitator has great effect on resistivity modification by ammonia. Since the critical temperature for ammonia is 132°C, condensation of ammonia is not expected to occur above this temperature. Therefore, ammonia injection will not change the ash resistivity above this temperature unless it is sorbed as a reaction product as NH₅SO..

The improvement in ESP performance upon ammonia injection is more likely due to space charge enhancement and improvement in cohesive force between the ash particles. The injected ammonia reacts with the existing sulfuric acid vapor, forming a fume of fine salt particles of ammonium bisulfate and sulfate. This fume creates a large surface area for collecting electrons. These charge carriers have a lower mobility than electrons and allows for a more stable corona, a higher electrical field strength without breakdown, and a higher specific power.

Ammonia is sometimes injected along with sulfur trioxide. Sulfuric acid condensation in the presence of ammonia (or ammonium bisulfate and sulfate) forms viscous surface deposits which increase the ash cohesivity and reduce particle reentrainment from the collection plates.

The emissions caused by ammonia injection are minimal. A significant part of the ammonia reacts with nitrogen oxides to form elemental nitrogen. Reaction between NH; and SO; also decreases the SO; emission.

Operating Problems

Ammonia conditioning could have the following operation and maintenance problems:

- 1. Plugging of injection nozzles.
- 2. Leakage and freezing of injection lines.
- 3. Dust build up on discharge electrodes of the ESP.

Economics

The capital and operating costs of ammonia conditioning, in December, 1982 U.S. Dollars, are \$0.21/kW and 0.022 mills/kWh, respectively.

Ammonium Compounds

Ammonium compound injection rate is in the range of 0.25 to 1.0 g/kg of coal burned. They are injected in solution form either upstream or downstream of the air preheater. Upstream is the preferred location because it offers long residence time and high temperature to vaporize or decompose the agent. However, upstream injection could cause plugging of the air preheater.

Ammonium compounds improve the ESP performance through the mechanisms of resistivity modification and space charge effect, but are not as effective as SO; in lowering the ash resistivity. Results show that they can lower the ash resistivity by about half an order of magnitude.

The injection of ammonium compounds causes increased sulfate and ammonia emissions. A particulate sulfate emission rate about

20 μ g/m³ and 1,500 μ g/m³ was measured without and with conditioning, respectively (Patterson et al., 1979C).

Problems

The most common operating problem with ammonium compound conditioning agents has been the plugging of the air preheater by deposits of reaction products when the agent is injected upstream of the air preheater.

Economics

There is no information on capital costs for an ammonium compound conditioning systems. The operating costs range from 0.024 to 0.052 mills/kWh (December, 1982 U.S. Dollars).

Organic Amines

Even though triethylamine is less volatile than ammonia, it can be injected in the vapor phase as well as in the solution form. Because it decomposes at high temperature, it is injected downstream of the air preheater.

The mechanism of triethylamine is not fully understood. The most likely mechanism is ash resistivity reduction. A pilot plant study by Brown et al. (1978) showed the resistivity decreased from 3 x 10° Ohm-m without conditioning to 5 x 10° ohm-m with a triethylamine dosage of 60 ppm. An independent pilot plant study by Bickelhaupt et al. (1978) showed similar results. With an injected concentration of 25 ppm of triethylamine, the resistivity decreased one to two orders of magnitude in the temperature range of 100°C to 150°C. It is more effective with lower temperatures, less basic ash composition, and greater concentration of the agent.

Triethylamine has only been studied in the laboratory and in pilot plants. There are no industrial users, so no economic data and user experience are available.

Dry Alkali

Sodium conditioning, unlike the other conditioning agents, is not limited to cold side ESP's. It can be added to the boiler along with coal or into the flue gas just ahead of the ESP. It can be applied either in solution form or in dry powder form. The most important parameter which affects its effectiveness is mixing of the sodium salt and the fly ash. To be effective, the sodium must either be incorporated into all the ash particles or co-precipitated with the ash on the precipitator plates so it yields well mixed deposits.

When the sodium is applied in dry powder form for coprecipitation, there may be difficulties in obtaining well mixed deposits. Lederman et al. (1979) applied the sodium in solution form and claimed that uniform coating of sodium salts on ash particles was obtained. When the agent is injected for coprecipitation with the ash, the dosage is 2% to 5% of the solids as Na₂O. The co-precipitated sodium compound should have a particle size distribution comparable to that for the ash.

In a pilot study, Gooch et al. (1981) added sodium compound to the coal supply prior to pulverization as a means of supplementing the sodium content of the fly ash. They speculated that complete decomposition and volatilization of the conditioning agent occurred in the boiler and subsequent condensation of the sodium compound was uniformly distributed and became an integral part of the fly ash surfaces.

Sodium is effective in reducing the fly ash resistivity if the sodium is mixed well with the ash. In situ resistivity measurements of co-precipitated ash showed the resistivity decreased from 2.1 x 10^{10} Ohm-m without conditioning to 3.7 x 10^{9} Ohm-m when conditioned with a 1.0 to 1.5% concentration of sodium carbonate as sodium oxide (Schliesser, 1979 a,b). A reduction of resistivity from 1 x 10^{10} to 1 x 10^{9} Ohm-m was measured by Gooch et al. (1980) when the sodium oxide content of the ash was increased to 2.5% from the inherent 0.3%.

Problems

Industrial users have only limited experience with sodium conditioning; therefore, operational problems are not well documented. However, there is one potential problem associated with the addition of sodium compound to the coal. The sodium may cause ash slagging and boiler fouling. In a properly operated system this should not be a problem.

Economics

The capital costs for a liquid solution conditioning system is about \$1.55 to 3.10/kW installed. The operating costs, excluding depreciation, is about 0.03 mills/kWh.

CONCLUSIONS

Of the many agents available, SO; is the most commonly used. SO; is effective in reducing the ash resistivity and will improve the ESP performance if particle resistivity is the limiting factor. The conditioning mechanisms of ammonia, ammonium compounds, and organic amines are not fully understood and the effectiveness of these compounds is not consistent.

Flue gas conditioning appears to be an acceptable and the least expensive option for upgrading the ESP performance for collecting high resistivity fly ash. However, before deciding on flue gas conditioning, the reasons for poor ESP performance should be determined. The poor performance could be due to factors other than high resistivity. Once the cause has been determined to be resistivity and conditioning has been chosen for retrofit, the conditioning system should be designed and operated with extreme care to avoid the harmful emissions due to conditioning agents.

Section 2 INTRODUCTION

CAUSES FOR UNSATISFACTORY ESP PERFORMANCE

ESP's have proved reliable, economic, and effective at controlling particle emissions from coal-fired utility boilers. Sometimes their performance has been unsatisfactory because of:

- 1. Coal composition change
- 2. More stringent particle emission regulations
- 3. Unstable electrical conditions
- 4. Changes in boiler and associated equipment operating conditions
- 5. Insufficient collection area
- 6. Poor gas distribution and maintenance.

Effects due to Coal Composition

ESP's are usually designed for boiler burning a specific coal. When a different coal, such as Western low sulfur, low alkali coal is burned, the ESP performance can change with changes in the following ash and flue gas properties:

- 1. Ash resistivity
- 2. Coal ash content
- 3. Ash composition
- 4. Ash particle size distribution
- 5. Moisture and fuel sulfur content

Ash Resistivity

The preferred ash resistivity, ρ , is in the range of $1 \times 10^{\circ}$ to $1 \times 10^{1\circ}$ Ohm-m. When particles of high resistivity ($\rho > 1 \times 10^{12}$ Ohm-m) are collected on the collection plates of an ESP, an insulating layer of ash forms there. Due to its high resistivity, charge dissipation is impeded by this layer. The voltage drop across this ash layer is increased and the field strength in the interelectrode region is decreased correspondingly. Thus, the particle charging rate falls, the driving force for the particle migration falls. Additionally

deposits are strongly electrostatically bound to the plates and are difficult to dislodge.

Trying to overcome the decreased field strength by raising the applied voltage to the discharge electrode can lead to the occurrence of back corona, which is the local breakdown or ionization of the gas molecules. Back corona occurs when the local field on the interstitial gas in the dust layer climbs to an excess of 1,000 to 2,000 kV/m. When back corona occurs, positive ions will stream out of the dust layer, quench the negative charges on the incoming particles, charge the particles, and force the particles back away from the plate. The back corona discharge can propagate through the interelectrode gas to the corona wire when the applied voltage is raised even higher. To prevent back corona, the operating voltage is lowered which in turn lowers the particle charging level.

If the ash resistivity is below 10⁵ ohm-m, charges dissipate readily and the voltage drop across the dust layer is low. The adhesion force on the collected particles is therefore low. The particles are more susceptible to being reentrained in the flue gas.

Ash Content

If the ash content of the coal is increased, then the mass of ash per unit of energy is increased and the ash burden entering the ESP will be higher.

Ash Composition

Depending on the composition of the ash, it may be conductive. The presence of sodium, lithium, and potassium in the ash increases its volume conductivity (Bickelhaupt, 1974). The particle surface composition can aid agglomeration of particles on collision with each other, or in keeping the particles on the plate from being reentrained (Tassicker, 1975).

Particle Size Distribution

The particle size distribution and mean particle size play a direct role in the efficiency at which particles can be collected. As the particle size decreases, particle migration velocity decreases and so does the collection efficiency of the ESP.

Another factor in the particle size distribution is the chemical make-up of the size fractions. Usually particles smaller than 5 μ m and especially the sub-micron segment are formed by condensation and are more spherical with minimal surface porosity. While these fine particles have greater surface area for a specific weight fraction, they also appear to sorb less of the condensible gases, especially SO, (Katz, 1979). Fine particles may also allow the collection surface deposit to increase in depth by the greater cohesion force of the particles (Katz, 1979).

Moisture Content

The hydrogen content and the amount of bound and free water in the coal determine the moisture content of the flue gas. High moisture, in conjunction with very low temperature, can improve the electrical conditions in the ESP and lower the ash resistivity. Water condensation and adsorption in the pores and on the surface of the ash particles leaches soluble compounds from the particles to form a layer of conductive or cohesive solution on the particle surface.

Fuel Sulfur Content

The sulfur in the coal is oxidized in the boiler to sulfur dioxide and sulfur trioxide. As the gas cools, sulfur trioxide associates with water vapor to form sulfuric acid vapor. This sulfuric acid condenses with the moisture in the flue gas to form a conductive layer on the particles, lowering the resistivity.

The SO₃ concentration in the flue gas depends on the fuel sulfur content, furnace operating conditions, and amount of metal

impurities, such as vanadium and iron, for converting SO_2 to SO_3 catalytically in the boiler.

Boiler and Associated Equipment Effects

Changes in the ratio of air to coal (excess air) changes the flue gas flow rate, temperature, and the properties of the fly ash produced. More air dilutes the particles and increases the flue gas flow rate, which in turn reduces the specific collection area. Oxidizing conditions in the boiler raise the melting temperature and viscosity of the fusible components of the fly ash (especially in wet-bottom boilers).

Flue gas temperature affects the electrical properties of the ash. Measurements have shown a variation in resistivity with gas temperature with a maximum around 150°C to 200°C (300°F to 400°F). High sulfur coal with low exit gas temperature produces low resistivity ash which may be too low for the ESP. On the other hand, low sulfur coal with high exit gas temperature results in high resistivity ash. For coals with less than 1% sulfur, the ESP should be operated at a temperature below 145°C (290°F). When coal sulfur content is higher than 2.5% the ESP should be operated at a temperature above 200°C (400°F) (Katz, 1979).

If the boiler is run over capacity, the temperature and amount of flue gas will be affected which in turn affects the ESP performance as discussed above. Deterioration of the performance of a control device upstream of the ESP (such as a cyclone battery or other mechanical collector) can cause substandard performance of the precipitator.

Insufficient Collector Area

The size or capacity of an electrostatic precipitator is expressed in terms of the specific collection area (SCA) which is the ratio of collection plate area to the flue gas volume flowrate. The units are $m^2/(m^3/s)$ or ft²/1,000 acfm. Precipitators built for efficiencies on the order of 90% for high sulfur coal have had specific collection areas of 20 to 40

 $m^2/(m^3/s)$. These same precipitators when used on lower sulfur coal ash have had much poorer performance. New precipitator installations are being designed to operate on lower sulfur fuels, and to meet higher performance standards. ESP's are presently designed with a SCA greater than 100 m²/m³/s to meet the New Source Performance Standards (NSPS).

METHODS FOR IMPROVING ESP PERFORMANCE

There are several methods for upgrading the ESP performance. . The options are:

- Add collection plate area to the existing ESP to overcome poor performance.
- 2. Use a wet electrostatic precipitator to minimize reentrainment and keep the plate clean.
- 3. Increase or lower the gas temperature in the ESP.
- 4. Add chemicals to modify the fly ash or the electrical conditions in the ESP.

For older ESP's, flue gas conditioning is often the most cost effective method of increasing the ESP performance. Several chemicals, such as sulfur trioxide, ammonia, ammonium compounds, organic amines, and dry alkalis, are presently used or proposed as conditioning agents. This report presents the results of a survey of flue gas conditioning agents and user experience.

Section 3 SULFUR TRIOXIDE CONDITIONING

CHEMICAL PROPERTIES

Sulfur trioxide is the most common flue gas conditioning agent used by power plants in the United States. It is a colorless, transparent, and stable liquid at room temperature and atmospheric pressure. It has a low vapor pressure. While it is not particularly corrosive in closed storage, it is highly hazardous if released in bulk.

If it is allowed to cool and solidify, three forms of SO: (alpha, beta, and gamma) may be formed. The lowest melting form (gamma) is preferred for handling, but is unstable. The higher melting solid (the alpha form) may form in the presence of moisture (Schrader, 1970). When exposed to humid air, the vapor quickly forms a dense fog of sulfuric acid (Archer, 1972).

The active conditioning agent in so-called "sulfur trioxide conditioning" is sulfuric acid. At the temperatures and humidities found at the air preheater outlet, sulfur trioxide is almost completely hydrated to sulfuric acid. Table 4 shows some important properties for SO; and sulfuric acid. Table 5 shows the equilibrium partition between SO;, SO;, and H₂SO.

H₂SO, has a low vapor pressure at room temperature and a strong affinity for water. Dissolved in water, at moderate concentrations it almost completely dissociates to two hydrogen ions and a sulfate ion. The hydrogen ions are small and mobile in solution. Their large number and mobility combine to make aqueous sulfuric acid solution electrically conductive.

The low vapor pressure of sulfuric acid means that strong solutions may be in equilibrium with very dilute vapor phase concentrations. In addition, the particle surface curvature increases the equilibrium vapor pressure (Nair and Vohra, 1975). Therefore, small acid drops can exist above the boiling temperature of a flat surface of the same acid composition. The low volatility and the high conductivity of sulfuric acid are responsible for its effectiveness in lowering fly ash resistivity in ESP's.

TABLE 4. PROPERTIES OF SULFUR TRIOXIDE*

| Property | <u>Sulfur Trioxide</u> | <u>Sulfuric Acid</u> |
|-------------------------|------------------------|----------------------|
| Melting Point, °C | | 10.6 |
| Gamma form (unstable) | 16.8 | |
| Beta form (unstable) | 35.8 | |
| Alpha form | 62.2 | |
| Vapor Pressure, kPa | | |
| 25°C | 35.3 | 0.702 x 10-* |
| 44.8°C | 101.3 | 3.62 x 10-3 |
| 218.3°C** | 8,470.0 | 24.9 |
| 272°C*** | | 101.3 |
| Density, kg/m³ | | |
| Liquid (20°C) | 1,920.0 | 1,830.5 |
| Vapor (20°C, 101.3 kPa) | 3.57 | 4.08 |
| Latent Heat, kJ/kg | 533.0 | 802.0 |
| Heat Capacity, J/(kg-K) | | |
| Average, 20-30°C | 322.0 | 384.0 |

*References: Schrader (1970), Perry & Chilton (1972), Gmitro and Vermeulen (1964).

****Critical Point**

***Aqueous sulfuric acid forms an azeotrope at 326°C, 101.3 kPa and 98.5 wt % H₂SO.. The normal boiling temperature shown is for pure liquid H₂SO..

TABLE 5. EQUILIBRIUM PARTITION OF SULFUR OXIDES^a (Dismukes, 1976)

| Temperature, | Relative concent | rations, % o | f sulfur comp | ounds |
|--------------|------------------|---------------|---------------------------------|-------|
| °C | SO 2 | SO; | H ₂ SO, ^b | |
| | | | | |
| 1,400 | 99.7 | 0.3 | 0.0 | |
| 1,000 | 97.6 | 2.4 | 0.0 | |
| 800 | 88.7 | 11.3 | 0.0 | |
| 600 | 42.2 | 57 . 7 | 0.1 | |
| 500 | 12.3 | 87.3 | 0.4 | |
| 400 | 1.6 | 94.8 | 3.6 | |
| 300 | 0.1 | 59.3 | 40.6 | |
| 200 | 0.0 | 6.5 | 93.5 | |
| 100 | 0.0 | 0.0 | 100.0 | |
| | | | | |

- a. Calculated from the data in JANAF Tables assuming concentrations of oxygen and water vapor equal to 4% and 10% by volume respectively.
- b. The maximum absolute concentration of each compound is sharply limited below 300°C as a result of the condensation of the predominant compound, H₂SO₁, in a binary H₂SO₁-H₂O liquid mixture.

CONDITIONING MECHANISM

Sulfuric acid reduces particle resistivity in electrostatic precipitators by forming a conductive layer on the surface of the particles. This layer forms by adsorption or condensation of sulfuric acid and water on the surface of the particles and in the crevices between particles on the collection plate.

CONDITIONING METHODS

Conditioning Agent Generation

Four processes are common for producing the sulfur trioxide for conditioning (Archer, 1972):

- 1. Vaporization of a sulfuric acid solution,
- 2. Vaporization of liquid sulfur trioxide,
- 3. Vaporization of liquid sulfur dioxide and oxidization to sulfur trioxide over a vanadium pentoxide catalyst.
- 4. Burning liquid sulfur in air to produce sulfur dioxide and then oxidize it to SO₃.

Other methods, such as stripping of oleum or in-situ oxidation of SO_2 in combustion gas are not commonly used.

Acid Vaporization

Sulfuric acid is heated to greater than 315°C (600°F). The vapor is then diluted with air and injected into the flue gas. A direct-fired heater is used to produce hot air with a temperature in the range between 315°C (600°F), where the acid may condense, and 600°C (1,100°F), where it dissociates. The hot air then contacts the acid in a vaporizer, which can be a packed tower or any other suitable direct contact heat-exchanger. The air flow rate is chosen to supply all the necessary enthalpy for vaporizing the maximum acid flow rate. The gas mixture from the vaporizer is maintained at a temperature above the acid dew point up to the injection point. Typical temperatures in the system are:

| Hot | air to vaporizer | 570°C | (1,050°F) |
|-----|--------------------|-------|-----------|
| Gas | from vaporizer | 450°C | (850°F) |
| Gas | at injection point | 400°C | (750°F) |

Catalytic Conversion of SO:

The catalytic conversion system includes an air heater, a SO₂ generator, and a catalytic converter. The air heater is a direct fired heater. SO₂ is produced either by burning liquid sulfur in air or by vaporizing liquid sulfur dioxide. The SO₂ gas is then mixed with hot air to obtain a maximum SO₂ concentration of about 8%.

The converter is a catalytic chamber with suitable catalysts, such as vanadium pentoxide. The inlet gas mixture at the catalytic chamber is at about 430 °C to 450 °C (800 °F to 850 °F). The oxidation of SO₂ to SO₃ is an exothermic reaction. Therefore, multiple passes with interstage cooling are employed to keep the temperature down and achieve good conversion efficiency.

The SO; rich stream from the converter has a temperature range from 450°C to 600°C (850°F to 1,100°F), which is much higher than the acid dew point. Thermal insulation on the injection duct will keep the injection temperature safely above the acid dew point even with moisture present.

Vaporization of Liquid SO,

Liquid SO, is metered into a vaporizer and then diluted with air. Dilution increases the volume for easier handling. The mixture must be conveyed in heated lines to the point of injection and is injected into the gas stream ahead of the precipitator.

Injection Location

The most common injection location is between the air preheater and the electrostatic precipitator inlet, for the following reasons.

- Injection_upstream of the air preheater increases the chance of acid condensation and corrosion there.
- Injection into a high temperature region can lead to the decomposition of sulfuric acid or sulfur trioxide into sulfur dioxide which is not an effective conditioning agent.
- 3. This position gives adequate residence time for

conditioning. SoRI (1972) determined that the fly ash could be satisfactorily conditioned in as little as 1 second after introduction of sulfur trioxide.

Southern Research Institute (SoRI) (1972) did tests on boilers which had mechanical collectors (batteries of cyclones) between the air preheater and the electrostatic precipitator. They found injection before or after the mechanical collector to be equally effective.

The temperature at the point of injection should be above the sulfuric acid dewpoint of the gas after addition (Reese and Greco, 1968) to prevent pre-mature condensation. The vapor should be allowed to mix with the flue gas and diffuse to the surface of the fly ash particles before condensation occurs.

RESULTS

Effects on Particle Resistivity

Table 6 and 7 show the ash resistivities measured with and without sulfuric acid conditioning. Figure 1 shows a summary of the effect of SO, conditioning on fly ash resistivity. In general, SO, conditioning is effective in reducing ash resistivity and improving the ESP performance if particle resistivity is the limiting factor. The dosage for SO, conditioning is normally in the range of 5 to 30 ppmv, but can be as high as 70 ppmv. An addition rate of 20 ppmv can lower resistivity by two orders of magnitude.

The effectiveness of sulfuric acid in reducing particle resistivity in ESP's depends on the gas temperature and ash composition. It is less effective at reducing resistivity at high temperatures (> 200°C) for two reasons. First, it is above the acid dew point such that there is either less adsorption or no condensation. Second, bulk or volume resistivity of the fly ash falls with temperature in the fashion of an Arrhenius relation (Bickelhaupt, 1974). At high temperatures, volume conduction becomes more important than surface conduction. The conductive sulfuric acid layer enhances surface conduction only.

The composition of the ash surface has an important effect on the amount acid required for conditioning. If the ash has a
TABLE 6. ASH RESISTIVITIES FOR USERS OF SO; CONDITIONING

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| Utility | Plant | SO; Dosage ppmv | <u>Ash Resistivit</u> without <u>SO</u> 1 | <u>y, Ohm-m</u> with <u>_SO</u> ; |
|--|---|-----------------------|---|---|
| City of Colorado Springs Dept. Pub. Util. | Drake | <60 | 5 x 10° | 6.5 x 10* |
| Commonwealth Edison | Crawford, Fisk, Joliet, Powerton, State Line, Waukegan, Will County | 5 to 30 | 10 ¹⁰ to 10 ¹¹ | 10• |
| Detroit Edison | Connors Creek, Harbon Beach, Marysville, Pennsalt, Port Huron, Trenton Channel | r 15 | | 107 to 10• |
| | Monroe (w: | 15 ith ll ppm NH,) | 10' to 10° | 10* (5x10' to 10* |
| Iowa Public Service | Neal | 20 | 1010 | 9 x 10' |
| Public Service Co | Arapahoe | 14 to 18 | 2x10 ¹⁰ to 10 ¹¹ | 2x10° to 10° |

TABLE 7. ASH RESISTIVITIES FOR SEVERAL USERS OF SO, CONDITIONING

| Reference | Utility, Plant | Fuel Sulfur wt % | SO₃ Dosage ppmv | Ash Resistivity SCA Ohm-m m²/(m³/s) | Coll. Effic. % |
|-----------------------------------|---|------------------------|--------------------------------------|--|------------------------|
| Trevor et al. (1963) | CEGB, Kincardine (Scotland, UK) | 0.5 | 0 5 10 15 | 0.4 to 2 x 10 ¹⁰ 0.25 to 1 x 10 ¹⁰ 1 to 5 x 10 ⁸ 0.6 to 2.7 x 10 ⁹ | 86 95 97.5 99 |
| Coutaller Richard (1967) | France | 0.5 | 0 15 20 | | 94.5 99.0 99.4 |
| Schrader (1970) | Germany | 0.8 to 0.9 | 0 14 to 26 | | 96.7 98.4 |
| Southern Research Institute | Pub. Svc. Co. Colorado Cherokee 2 | 0.6 | 0 13 27 | 1.6 x 10° 1.4 to 5.6 x 10° 2.5 to 5 x 10° | |
| (1972) | Utility X, Unit 4 | | 0 10 18 to 20 | 4.5 x 10° 2.3 x 10° | |
| | PSC Colorado, Cherokee 3 | 0.47 to 0.54 | 0 6 13 to 17 26 33 44 | l to 2 x 10 ¹⁰ 9.3 x 10 ⁹ 7.8 to 10 x 10 ⁹ 5.6 to 6 x 10 ⁹ 5 to 6.3 x 10 ⁹ 6.6 x 10 ⁹ | |
| | PSC Colorado, Arapahoe 4 | 0.49 | 0 6 12 18 | 3.8×10^{10} 5.7×10^{0} 3.2×10^{0} 1.9×10^{0} | |

TABLE 7. ASH RESISTIVITIES FOR SEVERAL USERS OF SO; CONDITIONING (Contd)

| Reference | Utility, Plant | Fuel Sulfur wt % | SO₃ Dosage ppmv | Ash Resistivity Ohm-m | SCA m²/(m³/g) | Coll. Effic. % |
|-------------------------------|--|------------------------|---------------------------------|--|------------------|--|
| SoRI (1972) (cont'd) | Utility Y, Unit 6 | 0.59 to 0.64 | 0 4 8 16 | 2 x 10 ¹⁰ 0.7 to 2.0x10 ⁹ 1.3 to 2.1x10 ⁹ 0.1 to 2.5x10 ⁹ | | |
| Green & Landers (1974) | PSC Colorado Arapahoe, Cameo, Cherokee | 0.6 to 0.7 | 0 18to25 | 1 x 10 ¹¹ | 17 to 43 | 54 to 94 73 to 96 |
| White (1974) | Calgary Pwr., Ltd. Sundance, Wabamum | 0.25 | 0 10 20 30 | 2 x 10 ¹⁰ 3 x 10 ¹ 4 x 10 ¹ 1 x10 ¹ | 25 18 | 71 97.5 |
| Cook (1975) | Commonwealth Edison, State Line | 0.5 to 0.9 | 0 20 30 35 40 50 | | 24 to 26 | 79 to 89 88 94 92 94 to 96 96 |
| Klipstein (1975) | Unnamed | | 0 16 30 39to55 | 10° to 10 ¹⁰ 2 to 7 x 10 ⁷ | | 78 to 81 84 to 89 94 94 to 96 |
| | | 2 to 3 | 0 | | | 95 to 97 |
| Cook & Trykowski (1976) | Commonwealth Edison, State Line | 0.5 to 0.9 | 0 40 | | 24 to 26 | 86 to 88 95.1 to 97.9 |

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| Reference | Utility, Plant | Fuel Sulfur wt % | SO; Dosage ppmv | Ash Resistivity Ohm-m | SCA m²/(m³/s) | Coll. Effic. |
|-------------------------------|---|------------------------|-----------------------|---|------------------|--------------------------------|
| Dismukes & Gooch (1977) | Iowa PS, Neal | 0.6 | 0 25 | 5.7 to 8.3x10 ¹⁰ 0.3 to 1 x 10 ⁹ | 39 | 91.3 99 to 99.2 |
| Brown et al. (1978) | Pilot Scale | | 0 5 13 64 | 10° 107 10° | | 85 91 99 98 to 99 |
| Patterson et al. (1979) | Unnamed | 0.8 1.1 | 0 32 | 1.7 x 10° 4.7 x 10° | 36 | 80.2 94.9 |
| Guiffre (1980) | Pennsylvania Pwr & Light, Montour & Brunner Island. | 1 2.2 | 0 19to25 0 | 5 x 10° | 35 35 | 78 to 80 94.5to94.8 93.6 |

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TABLE 7. ASH RESISTIVITIES FOR SEVERAL USERS OF SO; CONDITIONING (Contd)



CONCENTRATION OF SO3 INJECTED, ppm

Figure 1. Resistivity as a function of the concentration of injected sulfur trioxide. (Dismukes, 1976) large amount of alkaline compounds which react with or neutralize sulfuric acid, then a non-conductive salt layer will be formed. For basic ashes, a higher SO, dosage is needed so that excess acid can be adsorbed or condensed on top of the salts.

Emissions Caused By Sulfur Trioxide Conditioning

The major potential emissions caused by sulfur trioxide conditioning are sulfuric acid mist and particulate sulfate compounds. The emission rate will depend on the ESP performance, ash composition, and the gas temperature. Conditioning with SO, leads to the condensation of acid and the formation of sulfate on fly ash particles. Depending on the degree of improvement in the ESP particle collection efficiency with conditioning, an increase in sulfate emission may result.

The amount of alkaline compounds, specifically those of calcium, sodium, and magnesium, affect the split between free acid (as hydrated vapor or as adsorbed or deposited liquid) and sulfate bound to the particles. Chemical adsorption on, or reaction with the particle surface can decrease the amount of free acid present. Since sulfuric acid vapor is not collected by the ESP to any appreciable extent and the bound sulfates are, the more acid that the particles accept, the smaller the stack emission of acid will be. Fly ash surfaces which are alkaline favor such acceptance. Acidic ash surfaces (high Al₂O₃, low alkali) hinder such acceptance, and therefore are subject to large stack emission of acid (Dismukes, 1976; Dismukes and Gooch, 1977).

The precipitator temperature also affects the sulfate emissions. A temperature well above the acid dew point in the precipitator allows the acid to remain in the vapor. The acid vapor will nucleate and condense to form acid particles once it exits the stack and mixes with ambient air. If the precipitator temperature is close to or below the sulfuric acid dew point, then the injected SO₃ may still form a fog of sulfuric acid drops as well as condensing on the particles. Fog formation reduces available acid for conditioning and causes acid mist emission. Table 8 shows the results of field tests for the fate of

injected acid. The plant tested by Dismukes and Gooch (1977) (Iowa PS, Neal 2) had a basic ash. The precipitator temperature was low. Dismukes and Gooch showed a decrease in total sulfate emission with flue gas conditioning.

The plants tested by Patterson et al. (1979a) and Dismukes (1976) had an acidic ash and a higher precipitator temperature than the plant sampled by Dismukes and Gooch. They reported an increase in stack sulfate emissions with conditioning.

An increase of sulfate emissions from conditioning can be expected when the gas temperature approaches or is above the sulfuric acid dewpoint in the precipitator and the ash is acidic in character and does not absorb or accept the injected sulfuric acid. Sulfate emissions from conditioning are less for ash which is basic and has a high alkali content than that for acidic ash.

Effect On Particle Composition

The effect of flue gas conditioning on particle composition is shown in Table 9. The sulfate content of the fly ash increased with sulfuric acid conditioning. The increase depends on SO₃ dosage and is less when the sulfur-to-ash weight ratio is less.

<u>Bffect On Plume Opacity</u>

SO, conditioning may either increase of decrease the plume opacity. Many plants achieve an opacity of 20% or less with SO, conditioning due to increased particle collection by the ESP. However, an acid plume could be formed if the SO, dosage and the gas temperature are too high. Prudent operating procedure is to operate at a conditioning level where SO, or H.SO, is below the acid plume formation level.

Effect On Particle Size Distribution

Patterson et al. (1979a) measured the particle size distributions before and after conditioning. No detectable difference occurred because of:

1. The mass of SO, added is small in comparison with the ash (<1.0%);</p>

| | | | In | let | Ou | tlet |
|-----------------|-----------|----------|------------------|--------------------|------|---------|
| | | Injected | | Part. | | Part. |
| | Temp. | SO 3 | SO : | Sulfate | SO; | Sulfate |
| Reference | <u>°C</u> | ppmv | ppmv | mg/Nm ³ | ppmv | mg/Nm³ |
| | | | | | | |
| Dismukes (1976) | 125 | 0 | | | 1.5 | |
| | | 14 | | | 6 | |
| Dismukes & | 130 | 0 | 0.4 | 68 | 0 | 16 |
| Gooch (1977) | | 25 | 1.8 ^a | 123 | 0.9 | 6 |
| Patterson | 145 | 0 | 2.2 | 0.9 | 1.0 | 0.4 |
| et al. (1979a) | | 32 | 10.9 | 5.4 | 8.1 | 2.5 |

TABLE 8. FIELD DETERMINATIONS OF ACIDPARTITION IN FLUE GAS CONDITIONING

Note: 1 ppmv SO₁ = 4 mg/Nm³ of SO₄⁻⁻

a: The SO; injection rate is not a measured value and thus a large difference between injected and inlet SOE may be found. Also some SO; can be lost to dust and ducts.

| Reference | Utility, Plant | Added SO₃ ppmv | Particulate Mass Conc. mg/Nm ³ | Total Sulfate* wt % |
|-------------------------------|----------------------------|---------------------------|--|--|
| SoRI (1972) | PSC Colorado Arapahoe 4 | 0 6 12 18 | 1,100 to 5,000 1,100 1,100 1,100 1,100 | 1 to 1.5 2.23 2.5 2.97 |
| | PSC Colorado Cherokee 2 | 0 13 27 | 2,200 to 6,000 2,200 2,200 | 0.29 to 1.28 1.42 to 1.53 1.76 to 1.89 |
| | PSC Colorado Cherokee 3 | 0 13 26 33 44 | 6,000 900 900 900 900 900 | 0.57 to 0.77 0.9 1.09 1.00 1.12 |
| | Utility X | 0 10 18 to20 | 17,300 | 0.17 0.31 0.38 |
| | Utility Y | 0 4 8 16 | 7,000 | 0.24 to 0.27 0.29 to 0.35 0.34 to 0.41 0.36 to 0.51 |
| Dismukes & Gooch (1977) | Iowa PS Neal 2 | 0 25 | 6,000 to 6,300 6,900 | 0.76 avg 1.43 avg |
| Patterson et al. (1979a) | Unnamed | 0 32 | 2,100 to 3,100 2,100 to 4,200 | 0.05-0.07 0.14-0.18 |

TABLE 9.CHANGES IN PARTICLE SULFATE COMPOSITION
WITH SULFUR TRIOXIDE CONDITIONING

*Total of Free and Combined Sulfate

 Deposition of acid on the surface of the fly ash is only a few molecular layers thick.

Operating Problems

The earliest sulfur trioxide conditioning systems used liquid SO, as a raw material. Because of its volatility, hygroscopicity, and phase instability, it is hazardous to handle. The sulfuric acid solution vaporization method has corrosion problems. It is also difficult to turn down or shut down a sulfuric acid vaporizer without plugging the injection lines.

The systems which start with SO₂ or elemental sulfur have proved most reliable. Sulfur dioxide is less hazardous than SO₂, but is the most expensive source of synthetic SO₃ (Archer, 1972; Dalmon and Tidy, 1972). When elemental sulfur is available, it is the most economical source of SO₃.

In general, SO₂ and sulfur-based conditioning systems have offered availabilities in excess of 90 to 95%. Interviews of several users of SO₃ conditioning revealed the following categories of operating difficulties:

- 1. Corrosion.
- 2. Catalyst deactivation.
- 3. Over conditioning.

Sulfuric acid condenses in the lines leading to the injection nozzles if the wall temperature is below the acid dew point. These lines are prone to plugging during periods of slowdown, shutdown, or cold weather. The use of purge air in these lines is recommended during shut down periods.

Periodic changing of the SO₂ to SO₃ converter catalyst has been found necessary at one utility. The sulfur trioxide content of the injected gas decreases over about a year of operation. SO₃ concentration and ESP performance are restored after catalyst replacement. Catalyst deactivation may be responsible for the failure of sulfur trioxide conditioning in other installations.

It is possible to over-condition the ash. The presence of too much sulfuric acid in the flue gas can (Reese and Greco, 1968):

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- Lower the resistivity so much that the ash is reentrained from the collecting plates or bounces off them.
- Form a solution between the particles on the plates which binds them together and makes them difficult to dislodge from the plate.

USBR EXPERIENCE

The list of known past and present users of sulfur trioxide conditioning given in Table 10 were contacted for their experience. Summaries of user experience from those users who replied to our inquiries, appear below with other published information.

Colorado Springs Department of Public Utilities

The DPU has used a Research-Cottrell sulfur trioxide conditioning system on the Martin Drake plant for seven years. The efficiency of particle collection in the ESP increased 50% over the unconditioned case. The fly ash resistivity decreased by one order of magnitude.

Central Illinois Light

Central Illinois Light installed Wahlco sulfur trioxide conditioning systems at their Wallace plant in 1976. and they installed another Wahlco system at their Edwards plant in 1978.

Commonwealth Edison Company

Commonwealth Edison has installed 28 Wahlco sulfur burning trioxide flue gas conditioners at various plants. The oldest were installed in 1974. Test results from State Line units 1, 3 and 4 were reported by Cook and Trykowski (1976). The SO, dosage was about 40 ppmv. Compliance with emission limit was achieved at all but one of the units tested. That unit, number 3, had to be derated. Efficiencies of 96 to 97% were reported. The corresponding unconditioned efficiencies were about 85 to 88%.

TABLE 10. LIST OF PAST AND PRESENT USERS OF SULFUR TRIOXIDE CONDITIONING

| Company Name | Plant Name | FGC Licensor | References |
|--|-----------------|-------------------|------------------------------|
| Alabama Power Co. | Barry | Wahlco | |
| Central Illinois Light | E. D. Edwards | Wahlco | |
| Central Illinois Light | R. S. Wallace | Wahlco | |
| Cincinnati Gas & Electric Co. | W. C. Beckjord | Wahlco | |
| City of Colorado Springs DPU | Martin Drake | Research-Cottrell | |
| Cleveland Electric Illuminating Co. | Avonlake | Wahlco | |
| Cleveland Electric Illuminating Co. | Eastlake | Wahlco | |
| Cleveland Electric Illuminating Co. | Lake Shore | Wahlco | |
| Commonwealth Edison | Crawford | Wahlco | Cook (1975) |
| Commonwealth Edison | Fisk | Wahlco | Cook and |
| Commonwealth Edison | Joliet | Wahlco | Trykowski (1976) |
| Commonwealth Edison | Powerton | Wahlco | - |
| Commonwealth Edison | Waukegan | Wahlco | |
| Commonwealth Edison | Will County | Wahlco | |
| Commonwealth Edison/Indiana | State Line | Wahlco | |
| Consumers Power Co. | B. C. Cobb | Wahlco | |
| Consumers Power Co. | J. C. Weadock | Wahlco | |
| Detroit Edison | Conners Creek | Wahlco | Brennan and |
| Detroit Edison | Harbor Beach | Wahlco | Reveley (1977) |
| Detroit Edison | Monroe | Wahlco | |
| Detroit Edison | Marysville | Wahlco | |
| Detroit Edison | Pennsalt | UOP | |
| Detroit Edison | Port Huron | Wahlco | |
| Detroit Edison | Trenton Channel | Wahlco | |
| Duke Power | Belews Creek | Research-Cottrell | |
| East Kentucky Rural Electric Power Coop. | W. C. Dale | Wahlco | |
| Iowa Public Service Co. | G. W. Neal | Wahlco | Dismukes and Gooch (1977) |
| Lansing Board of Water & Electric Light | Erickson | Wahlco | |
| New York State Electric & Gas | Goudey | Wahlco | |
| New York State Electric & Gas | Greenidge | Wahlco | |
| Northern Indiana Public Service Co. | D. H. Mitchell | Wahlco | |

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TABLE 10. LIST OF PAST AND PRESENT USERS OF SULFUR TRIOXIDE CONDITIONING (Cont'd)

| Company Name | Plant Name | FGC Licensor | References |
|--|---|-----------------------------------|---|
| Ohio Edison Co. Pennsylvania Electric Co. | W. H. Sammis Front Street | Wahlco | |
| Pennsylvania Power & Light Co. Pennsylvania Power & Light Co. Pennsylvania Power & Light Co. | Brunner Island Montour Sunbury | Wahlco Wahlco Wahlco | Guiffre (1980) |
| Public Service Co. of Colorado Public Service Co. of Colorado | Arapahoe Cameo | Wahlco | Anon (1970) SoRI (1972) |
| Public Service Co. of Colorado | Cherokee | Lodge-Cottrell | Green and Landers (1974) White (1974) Brines and Reveley (1978) Midkiff (1979) |
| Tennessee Valley Authority UGI Corp. (Luzerne Electric) Upper Peninsula Generating Corp. Utah Power and Light Wisconsin Electric Power Co. | Bull Run Hunlock Creek Presque Isle Naughton Pleasant Prairie | UOP Wahlco Wahlco Wahlco | SoRI (1972) |

Detroit Edison

There are 17 Wahlco sulfur dioxide conditioning systems in the Detroit Edison network. Brennan and Reveley (1977) reported the following test results. At Marysville #11 there was a 10fold decrease in particle penetration through the electrostatic precipitator with addition of 20 to 30 ppmv sulfur trioxide. They meet the regulations with low sulfur coal.

Iowa Public Service Company

Iowa Public Service uses a Wahlco sulfur-burning sulfur trioxide conditioning system at George Neal, unit 2. Dismukes and Gooch (1977) reported the results of a performance test. In the last three years Iowa Public Service has attained:

- 1. A 100-fold decrease in particle resistivity.
- 2. A decrease of particle penetration from 9% to 1%.

They only have minor problems with the conditioning systems. The units run very close to the compliance limit and an outage of one transformer-rectifier set causes them not to comply.

Northern Indiana Public Service Company

NIPSCO has four Wahlco sulfur trioxide conditioning units, one (on Dean H. Mitchell, unit 6) has been in use since April 1980. They had satisfactory performance on Mitchell 6 for the first 8 months. Then intensified sparking and back corona were noticed. They switched to a low sodium coal and decreased the sulfur trioxide dosage from 40 ppm to 8 ppm. They have had satisfactory performance since then.

<u>Ohio Edison</u>

Ohio Edison has four Wahlco units at W. H. Sammis, units 1, 2, 3, 4. These became operational in 1981. Ohio Edison reports satisfactory performance on high resistivity ash when resistivity is the limiting factor in ESP performance.

Pennsylvania Electric Company

Penelec has been using sulfuric acid injection at their Front Street station for the last ten years. Acid injection is

used as required to attain compliance. They have experienced abnormally severe maintenance requirements.

Pennsylvania Power and Light

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PP&L had five Wahlco flue gas conditioning units installed in 1978 and 1979. They were installed at the following six locations:

Brunner Island 1 and 3

Montour 1 and 2

Sunbury 3 and 4

Testing (Guiffre, 1980) indicated that they could burn any coal and be in compliance at Brunner Island and Montour with a conditioning level of 25 ppm. Guiffre reported an increase in ESP efficiency from 90 to 95 percent and efficiency at the Montour station of 99.6%. The sulfur trioxide systems have good reliability.

Public Service Company of Colorado

PSCC is a pioneer in utility flue gas conditioning with sulfur trioxide. They have seven units which use sulfur trioxide or sulfuric acid.

<u>Arapahoe 1</u>. Unit 1 of the Arapahoe plant was converted to run on coal instead on natural gas. A new electrostatic precipitator was added with a Wahlco sulfur trioxide conditioning system. The system has been operating since 1977 and attains compliance with 25 ppm sulfur trioxide (Brines and Reveley, 1978).

Arapahoe 4. A UOP sulfuric acid vaporizer was installed on Arapahoe 4 in 1970 (Anon, 1970). There were many problems with the acid delivery system. SoRI (1972) reports a 100-fold decrease in ash resistivity with 6 ppm H₂SO.. Green and Landers (1974) report that even with conditioning, the ESP performance did not meet the revised guarantee. The observed efficiency was 77% when the guaranteed efficiency was 87%. The UOP system was replaced with a Wahlco conditioning system in 1979.

<u>Cherokee 2</u>. In 1971 PSCC installed a Lodge-Cottrell liquid sulfur trioxide vaporizer on their Cherokee plant, unit 2 boiler. SoRI (1972) reported a 10,000-fold decrease of particle

resistivity with 13 ppmv of sulfur trioxide conditioning. Also the electrical behavior of the ESP was better with conditioning. Green and Landers (1974) reported that the conditioned particle collection efficiency was 95.2% which is better than the guaranteed conditioned efficiency of 94.2%.

<u>Problems</u>. Green and Landers (1974) reported the following problems with PSCC's sulfur trioxide systems:

Condensation of acid in the ducts.
Ash buildup at the injection nozzles.

ECONOMICS

Table 11 shows the estimated costs of a sulfur trioxide flue gas conditioning installation as of December 1982. The capital cost is about \$5.15/kW and the operating cost is about 0.105 mills/kWh.

SUMMARY

Effectiveness

Sulfur trioxide (or its active equivalent, sulfuric acid) is the most widely used flue gas conditioning agent because it has been proven effective in those cases where particle resistivity is the limiting factor in electrostatic precipitator performance. High resistivity ash is most often the result of switching from high sulfur to low sulfur and low alkali coals.

Tables 6, 7, and 12 show that the addition of SO, reduces ash resistivity and increases ESP efficiency. Most of the power plants described above previously used high sulfur coal but now use low sulfur coal. They also use cold-side (<180°C) precipitators. Such utilities have had the most problems with poor precipitator performance (viz. Borsheim, 1977; Cook and Trykowski, 1976; Cragle, 1976; Dismukes and Gooch, 1977; Klipstein, 1975).

Cases of non-effectiveness of sulfuric acid conditioning stem from the following:

TABLE 11. ESTIMATED COSTS OF A SULFUR-BURNING SO; FLUE GAS CONDITIONING UNIT.

| Capital Costs (Installed), \$/kW | |
|----------------------------------|---------|
| Conditioning Eqpt. | \$ 4.12 |
| Dedicated Power (\$1000/kW) | 1.03 |
| | |

- Operating Costs, mills/kWh Sulfur at \$125/Mg 0.044 Electricity at (\$0.05/(kWh) 0.061
- Basis: 500 MW coal-fired utility. December, 1982 prices 40 ppmv design dosage 20 ppmv operating dosage 37.9% Plant thermal efficiency [9,000 BTU/(kWh) Heat Rate] 23 MJ/kg Coal Heating Value

Source: Wahlco, Inc.

| | | | | Effici | ency |
|-------------------------------|--|----------------|------------------|----------------|----------------------|
| Utility | Plant | Fuel Sulfur | SCA m²/(m³/s) | without SO3 | with SO; |
| Commonwealth Edison | Crawford, Fisk Joliet, Powerton State Line, Waukegan Will County | 0.5 | 24 to 26 | 87 | 98 |
| Detroit Edison | Connors Creek,Harbor Beach, Marysville, Pennsalt, Port Huron, Trepton Channel | 0.5 to 0.7 | | 85 to 90 | |
| | Monroe | 2.3 (Blend) | 37 9 | 97.5 to 98.5 | 99.8* |
| Iowa Public Service | Neal | 0.6 to 0.7 | 39 | 91 | 99 |
| Public Service Co Colorado | Arapahoe | 0.6 to 0.7 | 20 to 30 | 60 to 86** | 14 to 50 (mg/Nm³) |

TABLE 12. ESP PERFORMANCE FOR SEVERAL SELECTED USERS OF SO; CONDITIONING

*Combined Ammonia and Sulfur Trioxide Conditioning **Reference: Green and Landers (1974)

- 1. The conditioner supply may malfunction. The lines may plug or the SO₂ conversion may fall.
- 2. The precipitator performance may be limited by other phenomena besides resistivity. The transformer/rectifiers may be undersized. The superficial velocity may be too high causing reentrainment. The velocity distribution may be too irregular.
- 3. The temperature may be so low that acid condensation occurs at the injection point.
- The temperature may be so high (>200°C) that surface conduction is not important.
- 5. The ash resistivity may already be satisfactory (approx. 10* Ohm-m).

Problems

It is possible to over-condition the ash. The presence of too much sulfuric acid in the flue gas can:

- Lead to acid particle nucleation before mixing with the flue gas.
- 2. Lower the resistivity so much that the ash is reentrained from the collecting plates or bounces off them.
- 3. Form a solution between the particles on the plates which binds them together and makes them difficult to dislodge from the plate.

Most SO; conditioning systems have given 95% or higher availability. The most reliable designs have been the ones which use elemental sulfur and those which use sulfur dioxide even though it is not commonly used.

Section 4 AMMONIA CONDITIONING

Ammonia conditioning has been used successfully in Australia. There the coals have very low sulfur (0.3 to 0.7 weight percent) and produce high resistivity ash (as high as 10¹² Ohm-m). Because of the success in Australia much research has been done on ammonia conditioning in the U. S., yet there are few users here.

CHEMICAL PROPERTIES

Ammonia is a vapor at room conditions. Table 13 shows the properties of ammonia. The critical temperature is 132°C. Above this temperature ammonia does not boil or condense. Therefore, condensation on the fly ash would not be expected to occur with ammonia above 132°C, although physical adsorption might.

Because of the high volatility of ammonia, it is injected in the vapor form under its own vapor pressure. In Australia, ammonia is also injected in solution form (McLean, 1976; Tassicker, 1975; Watson, 1976; Walker and Lamb, 1978). A concentrated ammoniacal liquor (CAL) by-product is available from steel making operations. CAL contains about 17% ammonia (as ammonia) by weight, both free and in the form of various salts, notably chloride and bicarbonate.

CONDITIONING MECHANISM

The way in which ammonia affects the performance of electrostatic precipitators is not completely understood. Dismukes (1975) reports the following effects:

1. Space charge enhancement. Ammonia reacts with the sulfuric acid vapor present in the gas, forming a fume of fine salt particles of (NH₄)₂SO₄ and NH₄HSO₄. The electrons and ions from the corona collide with and reside on the fine particles. The mobility of these charged particles is less than the ions, therefore the current density falls.

TABLE 13. PROPERTIES OF AMMONIA*

| Melting Point, °C | -78 |
|---------------------|----------|
| Vapor Pressure, kPa | |
| -33°C | 101.3 |
| 25°C | 1010 |
| 132.4°C** | 11,300** |

| Density, kg/m³ | |
|------------------------------|------|
| Liquid (20°C) | 610 |
| Vapor (20°C, 101.3 kPa) | 0.71 |
| Latent Heat (at -33°C) kJ/kg | 1373 |
| Heat Capacity, J/(kg-K) | |
| Avg, 20-30°C | 670 |

*Reference: Perry and Chilton (1972)

****Critical State**

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The "gas phase resistivity" increases, thus the voltage drop across the interelectrode gap rises and the voltage drop across the dust layer falls. The field in the interelectrode space is raised and the chance of electrical breakdown in the dust layer is decreased. This allows operation at higher applied voltages.

2. Increased cohesiveness. Sulfuric acid condensation in the presence of ammonium sulfate or bisulfate leads to adsorption of acid and salts to water on the surface. These surface deposits are viscous and sticky, which increases cohesion between neighboring particles in the dust layer on the collection plates and reduces reentrainment.

Because of the uncertainty of such things as natural SO, concentrations in the gas, quantification of the above effects has been unpredictable.

INJECTION LOCATION

Ammonia can be injected either before or after the air preheater. At Colorado Ute Electric Association, Hayden 1 and 2, it is injected upstream of their hot side ESP. With injection at this location the air preheaters require washing roughly twice a year to avoid plugging with deposits of reaction products.

Reese and Greco (1968) tried ammonia injection upstream of the air preheater at several plants at TVA. They experienced air preheater plugging. The plugging problem was eliminated by injecting the ammonia downstream of the air preheater. The precipitator efficiency due to this relocation of injection location was about the same.

Baxter (1968) also used ammonia injection upstream of the air preheater. If the temperature in the air preheater were above 200°C no plugging occurred. Cooler temperatures brought plugging.

In Australia, where ammonia is the most popular conditioning agent, ammonia was injected downstream of the air preheater at all the ammonia conditioning installations (Watson, 1976).

RESULTS

Particle Resistivity

The success of sulfur trioxide conditioning with resistivity related malperformance prompted investigations of resistivity modification by ammonia. Tables 14 and 15 show a summary of the results.

The ability of ammonia to alter resistivity is not clear. Ammonia conditioned resistivities can be less than, the same as, or greater than the unconditioned values. The temperature of the precipitator has great effect on the sensitivity of the ash to resistivity modification by ammonia. Ammonia is more effective at low temperature (<110°C).

In two cases, Stations "Cl" and "C2" reported by Baxter (1968) and at Detroit Edison Monroe 1 and 2, the addition of ammonia raised the resistivity. In the case reported by Baxter, the temperature was low and the resistivity before conditioning was very low because of adsorbed or condensed sulfuric acid. The injected ammonia neutralizes the acid and thus increases particle resistivity.

The case of Detroit Edison-Monroe is not so clear. This plant uses a medium sulfur blend of high sulfur Ohio coal and low sulfur Kentucky coal. Simultaneous ammonia and sulfur trioxide injection is used at Monroe. The addition of sulfur trioxide lowers the resistivity to about 10° Ohm-m, which is too low and can lead to increased particle reentrainment. The addition of ammonia alone or in conjunction with sulfur trioxide raised the particle resistivity at Monroe.

The data of Baxter (1968), McLean (1976)), Bickelhaupt et al. (1978), and Brown et al. (1978) show ammonia conditioning decreases the particle resistivity. McLean shows one case with a four order of magnitude decrease in resistivity with ammonia conditioning. Bickelhaupt and coworkers found that only acidic ash responded to resistivity modification by ammonia, and then only at low temperatures (<110°C). The work of Bickelhaupt et al. did not take into account the effect of sulfur oxides on this process. Brown et al. (1978) found that the resistivity of the

| Reference | Utility, Plant | Fuel Sulfur wt % | NH₃ Dosage ppmv | Ash Resistivity Ohm-m | Spec. Coll. Area <u>m²/(m³/s)</u> | Coll. Effic. | Temp. <u>°C</u> |
|--------------------------|----------------------------------|------------------------|--|-------------------------------------|---|---|--------------------|
| Baxter (1968) | Station "A" | Low | 0 15 | 10 ¹⁰ 10 ⁹ | | 85 ^a | 204 |
| | Station "B" | Low | 0 15 | 10 ¹ ° 5x10° | | 40 ^a | 149 |
| | Station "Cl" | Med. | 0 15 | 5x10° 10° | | 70 ^a | 143 |
| | Station "C2" | Med. | 0 15 | 5x10* 10* | | 30 ^a | 143 |
| | Station "D" | Med. | 0 15 | 3x10• 5x10• | | 60 ^a | 204 |
| Reese Greco (1968) | TVA, Widow's Creek Colbert | 2.5 to 3.5 | 0 5 7.5 15 25 75 | | 20 to 24 | 57 80 to 86 84 to 89 92 92 97 | 132 |
| Dalmon Tidy (1972) | Laboratory | Low Sulfur Oil | 0 50 180 0 ^C 200 ^C | | , | 0.095 ^b 0.123 ^b 0.180 ^b 0.136 ^b 0.14 ^b | 150 |

^aPercent decrease of particle concentration over unconditioned case ^bEffective migration velocity, m/s ^cWith 300 ppmv SO₂

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| Reference | Utility, Plant | Fuel Sulfur & | NH; Dosage ppmv | Ash S Resistivity Ohm-m | Spec. Coll. Area m²/(m³/s) | Coll. Effic. | Temp. °C |
|---|--------------------------------|----------------------|--|---|----------------------------------|---|---|
| Dalmon Tidy (1972) cont'd | Laboratory | Low Sulfur Oil | 10 ^d 180 ^d 10 ^e 180 ^e | | | 0.151 ^b 0.16 ^b 0.145 ^b 0.161 ^b | · · · · · · |
| McLean (1976) | ECNSW (Australia) | 0.3 to 0.4 | 0 40 to 5 | 10 ¹¹ | | 0.06 ^b 0.08 ^b | |
| | Mobile Pilot ESP | 0.36 | 0 40 | 3x10 ¹ 2 <<10 ⁸ | 30 to 72 | 0.07 ^b 116 0.09 ^b | to 149 |
| • | | 0.3 to 0.4 | 0 55 | 1011 | | 0.04 ^b 0.08 ^b | |
| | | 0.6 to 0.7 | 0 50 | 2x10 ¹ ² | | 0.05 ^b 0.06 ^b | |
| | | 0.4 | 0 17 | >1012 | | 0.037 ^b 0.06 ^b | |
| Southern Research Institute (1972) | TVA, Widow's Creek "B" 7 | 3.59 | 15 0 7 15 15 15 15 0 15 | 2x10* 4x10* 3x10* 3x10* 2x10* 2x10* 5x10* 3x10* 6x10* | 25 | | 124 127 135 137 139 141 142 143 143 |
| Effe dwith | ctive Migration | Velocity | , m/s | | | | |

With 100 ppmv HCl With 300 ppmv SO, and 100 ppmv HCl

| Reference | Utility, Plant | Fuel Sulfur wt % | NH₃ Dosage ppmv | Ash Resistivity Ohm-m | Spec. Coll Area m ² /(m ³ /s | Coll. Effic. | Temp. °C |
|-------------------------------|-----------------------------------|------------------------|---------------------------|--|--|--|--------------|
| Potter & Paulson (1974) | CSIRO (Australia) Pilot ESP | 0.5 | 0 20 | | 45 | 92 96 | 120 |
| Dismukes (1975) | TVA, Widow's Creek | 0.9 3.5 | 0 10 0 20 | 4x10° 4x10° 1x10° 3x10° | 20 to 24 | 90 98 87 >99 | 132 |
| | Bull Run | 1.2 | 0 7 | 3x10 ^s 4x10 ^s | 28 | Unchanged | 127 |
| | Gallatin | 4 | 0 20 | 4x10• 3x10• | | 350f 70f | 143 |
| Tassicker (1975) | ECN <i>S</i> W (Australia) | 0.4 | 0 >0 >0 >0 >0 | | 52 to 60 70 to 80 95 110 55 to 60 | 60 to 80 97 to 98. 99 to 99. 99.5 98.9 to 99 | 5 5 .1 |
| Ashton (1976) | Pacific Pwr & Light, Bridger | 0.6 to 0.7 | 0 >0 | No Effe No Effe | ect | No Effect No Effect | |
| Watson (1976) | ECNSW (Australia) | 0.6 | 0 >0 | | 74 | 94 97 to 98 | 116 |

fParticle Concentration, mg/Nm³

| Reference | Utility, Plant | Fuel NH; Sulfur Dosage Re wt % ppmv | Ash Spec. Coll. sistivity Area Ohm-m m ² /(m ³ /s) | Coll. Effic. Temp. <u>%</u> °C |
|-------------|-------------------|---|--|--------------------------------------|
| Bickelhaupt | Laboratory | Hi #1 0 | 1x10 ¹⁰ . | 110 |
| et al. | | 37 | 3x10* | 110 |
| (1978) | | 100 to 120 | 4x10• | 112 |
| | | 0 | 2x10 ¹⁰ | 144 |
| | | 100 to 120 | 9x10* | 144 |
| | | 0 | 4x10° | 352 |
| | | 100 to 120 | 4x10* | 352 |
| | Laboratory | Hi #2 0 | 8x10* | 112 |
| , | | 37 | 7x10* | 110 |
| | | 100 to 120 | 3x10* | 112 |
| | | ` 0 | 2x10* | 144 |
| | | 100 to 120 | 10. | 144 |
| | | 0 | 3x10' | 352 |
| | | 100 to 120 | 3x10' | 352 |
| | | Lo #1 0 | 6x10' | 70 |
| | | 100 to 120 | 8x10* | 70 |
| | | 0 | 4x10 ¹⁰ | 110 |
| | | 37 | 4x10 ¹⁰ | 110 |
| | | 100 to 120 | 7x10° | 112 |
| | | 0 | 8x10 ¹⁰ | 144 |
| | | 0 | 10' | 352 |
| | | 100 to 120 | 10' | 352 |
| | | Lo #2 0 | 2x10* | 110 |
| · | | 37 | 2x10* | 110 |
| | | 118 | 2x10* | 110 |

| Reference | Utility, Plant | Fuel Sulfur wt % | NH₃ Dosage ppmv | Ash Resistivity Ohm-m | Spec. Col Area <u>m²/(m³/</u> | 1.Coll.Effic.(s)8 | Temp. <u>°C</u> |
|-----------|-------------------|------------------------|-----------------------|-----------------------------|-------------------------------------|-----------------------|--------------------|
| Brown | Pilot Plant | 0.3 | 0 | 3x10* | | 85 | |
| et al. | | | 5 | 2 to 5x10° | | 87 | |
| (1978) | | | 50 | 1 to 5x10* | | 88 to 90 | |
| | | | 78 | 3 to 7x10* | | | |
| Walker | ECNSW | 0.3 to | 0 | | | 0.2to0.4 ^b | 90to125 |
| Lamb | (Australia) | 0.7 | 20to30 | | | 0.4to0.6b | 90to130 |
| (1978) | | | 0 | | · | 0.2to0.3b | 162to210 |
| | | | 20to30 | | | 0.3to0.6 ^b | 150to205 |
| Katz | Case "B" | 2.3 | 0 | | 26 | 71.6 | 119 |
| (1979) | | 2.8 | 0 | | 26 | 63.4 | 139 |
| | | 2.8 | 10 | | 26 | 84 | 139 |
| | | 2.3 | 0 | | 26 | 98 | 163 |
| | | 2.3 | 32 | | 26 | 96.5 | 163 |
| | Case "C" | 1.73 to | o 0 | | 42 | 96.1 | 132 |
| | - | 1.76 | 12 | | 42 | 99.2 | 132 |
| | | | 4.5 | | 42 | 99.4 | 141 |
| Castle | Australia | Low | 0 | | 45 | 91 to 92 | |
| (1980) | | | 20 | | | 96 | |

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| Utility | Plant | Fuel Sulfur & wt | Added NH3 ppmv | Ash C Resistivity Ohm-m | Specific ollection Area m ² /(m ³ /s) | Coll. Effic. |
|-------------------------------|------------------------|------------------------|---|-------------------------------------|--|---------------------|
| Colorado-Ute Elect. Assoc. | Hayden | 0.5 | 0 100 | | | 97.8 99.4 |
| Detroit Edison | Monroe 1,2 | 2.3 (Blend) | 0 11 to 12 11 to 12 15 ppmv SO,) | 3x10" 0.3 to 6x10 0.5 to 1x10 | 37 9 [.] • | 7.5 to 98.5 99.8 |
| Tennessee Valley Authority | Widow's Creek "B" 7 | 3 to 3.5 | 0 10 to 15 | | 25 | 75 85 to 90 |

ash decreased at first with small amounts of ammonia, but addition of more ammonia showed no change.

Two tests of the Tennessee Valley Authority's plants showed little or no effect of ammonia conditioning on ash resistivity. Southern Research Institute (1972) reported that the resistivities correlated with temperature but not with ammonia dosage at TVA's Widow's Creek plant with high sulfur coal. Dismukes (1975) showed no effect of ammonia conditioning at the same plant on both high and low sulfur coal, and at the Bull Run and Gallatin plants on medium and high sulfur coals.

Emissions Caused by Ammonia Conditioning

Spafford et al. (1979) did experiments on the fate of ammonia in a laboratory ESP and a flue gas train setup without fly ash. A summary of the data is shown in Table 16. They found the following:

- A significant part of the ammonia (20 to 30 ppm out of 63 ppm added) reacted with nitrogen oxides. The reaction product is probably elemental nitrogen.
- 2. In the presence about 30 ppmv SO:, a stoichiometric amount of the ammonia reacted with sulfuric acid to form ammonium bisulfate aerosol. Practically all of this aerosol was collected by the ESP. The effective ion mobility in the ESP decreased (a space charge effect).
- 3. In the presence of low amounts (1 to 2 ppm) of SO,, the ammonia neutralized the sulfuric acid, but no change in electrical conditions was noticed.

The Southern Research Institute (1972) and Dismukes (1975) performed field tests to determine the destination of the ammonia injected at TVA plants. Their data also appear in Table 16. The tests of SoRI (1972) found negligible ammonia in the fly ash. They also could not account for all the ammonia injected. The recoveries were less than 50%.

In the test described by Dismukes (1975), there was a reasonable material balance on the ammonia. Almost all of the ammonia ended up in the solid phase before it reached the

TABLE 16. PARTITION OF ADDED AMMONIA BETWEEN GAS AND PARTICLES

| | | b ab b A | <u>Gas</u> P | nase | <u>Particle</u> | Phase |
|---------------------|------------------------------|-------------------|-------------------|---------------------------------|---------------------|---------------------|
| | Temp. | NH I | SO1 | NH 3 | so,ª | NH , |
| Reference | °C | ppmvb | ppmv ^b | ppmv ^b | mg/Nm ^{3b} | mg/Nm ^{3b} |
| Southern | 142 | 0 | 15 | 0 | 70to80 | 0 |
| Research | 135 | 7 | 13to15 | 0.2 | 80to120 | <2 |
| Institute (1972) | 140to143 | 15 | 10tol8 | 0.4 | 88to97 | <2 |
| | | | | | | |
| Dismukes | 132 | 0 | 5 | 0.6 ^C | 33 | <1.5 |
| (1975) | | 10 | 1 | 0.8 | 30 | 6.7 |
| | 127 | 0 | 2 | <0.3 | | |
| | | 7 | 1 | <0.3 | | |
| | 132 | • 0 | 11 | <0.1 | 117 ^d | <1 ^d |
| | | 20 | 3 | <0.1 | 123 ^d | <11 ^d |
| | 143 | 0 | 9 | <0.1 | | |
| | | 20 | 1 | 1.0 | | |
| Spafford | 175 | 29 | 0 | 1.9 | 104 | 19 |
| et al. ^e | | | 2 | 0.1 | 100 | 15 |
| (1979) | | | 7 | 0.4 | 88 | 13 |
| | 100 | 29 | 0 | 0.3 | 0 ^t | 0.7 [±] |
| | | | 0 | 0.2 | 0 ^t | 1.1* |
| | | | 0 | 0.3 | 100 | 15 |
| | | | 0 | 0.3 | 108 | 22 |
| | a _{Total} | Sulfate | . Sum a | of bound | sulfate | and free acid. |
| , | ^b l ppmv | NH 3 = | 0.75 mg/ | Nm ¹ NH ⁺ | | |
| | 1 ppmv | $SO_3 =$ | 4 mg/ | Nm ³ SO. | | |
| | ^C Anomal | ous val | ue due t | o leaka | ge of amm | onia |
| | condit | ioning | equipmer | nt. | | |
| | ^d Based SoRI (| on an a 1972). | ssumed] | loading | of 9,400 | mg/Nm³ as in |
| | ^e Labora | tory si | mulatior | with s | ynthetic | flue gas and |
| | f_{A+} +he | 00+10+ | of an e | neraize | d ESP. | • • |
| | | JULIEL | | | A DOL! | |

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electrostatic precipitator. There was also marked reduction of the SO₃ entering the ESP.

The results of Dismukes (1975) and Spafford et al. (1979) reveal that the sulfur trioxide vapor emission from the plant would be decreased with the addition of ammonia and that most of the ammonia and all of the sulfate particles were removed in the ESP.

Effect on Particle Composition

A summary of the investigations of particle composition change is given in Table 17.

The Southern Research Institute (1972) analyzed ash from the inlet of the ESP in TVA Widow's Creek and found the sulfate contents correlated with temperature only, not with added ammonia concentration. The ammonia in the ash was negligible.

Dismukes (1975) analyzed the ash from several TVA plants and found no change in pH with ammonia conditioning. Contrary to SoRI's findings at the same plant earlier (1972), Dismukes also found significant increase in the particle ammonia content with ammonia conditioning.

Baxter (1968) determined the equilibrium acidities of ash from several facilities which use ammonia conditioning and found the ash was acidic in all cases. It seems that ammonia always raises the pH of the ash.

Effect on Particle Size Distribution

The effect of ammonia conditioning on particle size distribution is not known because the outlet particle size distributions with and without conditioning have not been published. Dismukes (1975) reported the formation of fumes at the inlet of the precipitator with ammonia injection. The total number of nuclei in the 0.005 to 1.0 μ m diameter range increased about 3 times with ammonia conditioning (Table 18). Spafford et al. (1979) speculated that the aerosol is ammonium bisulfate.

TABLE 17. CHANGES IN PARTICLE COMPOSITION DUE TO AMMONIA CONDITIONING

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| | | | <u>Inlet Pa</u> | rticle J | Properti | es |
|------------|---------------|-------|--------------------|----------|----------|--------|
| | Inj | ected | | | | |
| | | NH 2 | Loading | s0, | NH + | |
| Researcher | Utility | ppmv | mg/Nm ³ | % wt | % wt | PH |
| Baxter | Station "A" | 0 | | | | 5.5 |
| (1968) | | 15 | | | | 7 |
| | Station "B" | 0 | | | | 5 |
| | | 15 | | | | 6 |
| | Station "C" | 0 | | | | 3.5 |
| | | 15 | | | | 4.5 |
| | Station "D" | 0 | | | | 3 |
| | | 15 | | | | . 4 |
| Southern | TVA, Widow's | 0 | 9,400 | 0.73t | o <0.02 | 11.0 |
| Research | Creek | | | 0.88 | | |
| Institute | | 7 | 9,400 | 0.87ta | o <0.02 | 10.5to |
| (1972) | | | | 1.29 | | 10.9 |
| | | 15 | 9,400 | 0.86tc | o <0.02 | 9.5to |
| | | | | 1.21 | | 10.6 |
| Dismukes | TVA | 0 | 15,200 | 0.22 | <0.01 | 5.2 |
| (1975) | Widow's Creek | 10 | 16,700 | 0.18 | 0.04 | 5.4 |
| | | 0 | | 1.24 | <0.01 | 10.0 |
| | | 20 | | 1.31 | 0.12 | 10.0 |
| | Bull Run | 0 | | 0.31 | <0.01 | 4.5 |
| | | 7 | | 0.33 | 0.05 | 4.4 |
| | Gallatin | 0 | | 1 | <0.01 | 8.6 |
| | | 20 | | 1.4 | 0.21 | 8.6 |

| Plant | Ammonia ppmv | Nucleus Concentration m ⁻³ |
|---------------|-----------------|---|
| TVA Bull Run | 0 | 2.4x10 ¹² |
| | 7 | 9.8x10 ¹² |
| Widows' Creek | 0 | 1.2x10'' |
| | 20 | 3.1x10 ¹³ |
| Gallatin | 0 ′ | 2.2x10 ¹³ |
| | 20 | 6.1x10 ¹³ |

TABLE 18.CHANGE OF PARTICLE NUMBER CONCENTRATION WITHAMMONIA CONDITIONING (Dismukes, 1975)

Operating Problems

Investigators in Australia (Walker, 1977, Watson, 1976; McLean, 1976) reported the following operating and maintenance problems:

- The normal problems associated with pressurized gases, such as: leaks, vaporizer freezing in cold weather, freezing of water in the lines.
- The injection nozzles may plug during periods of extended shutdown because of buildup of dust and ammonium carbonate deposits. The use of purge air prevents this buildup.
- 3. Deposits are noticed on the discharge electrodes of the ESP. They are "sausage-like shapes or spikes of hard dust" (Walker and Lamb, 1978).

Effect on Plume Opacity

Dismukes (1975) reported oscillation in the opacity at the TVA-Gallatin plant before conditioning with ammonia. The opacity oscillation followed the rapping cycle of the ESP and slowly vanished after injection of ammonia.

Changes in the opacity oscillations were not clearly evident until approximately 30 min after startup of the conditioning system. After two hours the opacity reached steady-state. When injection of ammonia stopped, the opacity increased and the oscillations from rapping returned after 2 hr.

<u>Bffect on Particle Cohesivity</u>

According to Dismukes (1975), photomicrographs of the fly ash showed particles bridged by a feathery material thought to be ammonium sulfate. Cascade impactor studies indicated that the conditioned particles bounced less.

ECONOMICS

Reese and Greco (1968) reported the installation costs for ammonia injection facilities at TVA. The costs were updated to December, 1982 U.S. Dollars based on Chemical Engineering Plant Cost Index and are presented in Table 19. The capital and

TABLE 19. ECONOMICS OF AMMONIA CONDITIONING Capital Costs, \$/kW Conditioning Equipment \$0.16 Dedicated Steam Facilities 0.05 at \$240,000/(Mg/hr)

- Operating Costs, mills/kWh Ammonia at \$325/Mg \$0.018 Steam at at \$12.30/Mg 0.004
- Basis: 550 MW coal-fired utility December, 1982 prices 100 ppmv design dosage 50 ppmv operating dosage 37.9% Plant thermal efficiency (9000 BTU/(kWh) Heat Rate) 23 MJ/kg Coal Heating Value

References: Reese and Greco, 1968;
operating costs are \$0.21/kW of plant capacity and 0.022 mills/kWh.

USER EXPERIENCE

Table 20 is a list of ammonia conditioning users. A summary of user experience is presented in the following paragraphs.

Cleveland Electric Illuminating Co. (CEI)

Ammonia conditioning has been used at the CEI Avon Lake and East Lake plants for about four years. The coal is a variable blend of high sulfur Ohio coal and low sulfur Pennsylvania coal. The precipitators were guaranteed for 99.5% efficiency and have SCA (specific collection areas) of 37 m²/(m³/s) (190 ft²/1,000 acfm) at Avon Lake and 44 m²/(m³/s) (225 ft²/1,000 acf) at East Lake.

Ammonia conditioning is used as required to obtain compliance with the particulate regulations. East Lake complies with the particulate regulations only part of the time. They are forced to limit coal feed to the boiler (therefore reducing power production) to meet the compliance requirements. Avon Lake is not in compliance, even with ammonia conditioning. CEI plans to add another precipitator in series at Avon Lake.

In general CEI would rather not depend on flue gas conditioning at their plants in order to meet the pollution regulations. The precipitators they are planning to install on future projects will have a minimum SCA of 120 m²/(m³/s) (600 ft²/1,000 acf), especially if low sulfur coals are burned.

Colorado-Ute Electric Association

Colorado Ute has used ammonia at their Hayden units 1 and 2 for three years. These are hot side ESP's. Their dosage ratio is 1 ton of ammonia per 2,700 MW-hr (about 100 ppmv). The particle mass collection efficiency has improved from 97.8% to 99.4%. Their fuel is 0.5% sulfur coal.

TABLE 20. LIST OF PAST AND PRESENT USERS OF AMMONIA

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| Company Name | Plant Name | FGC Licensor | References |
|-------------------------------------|------------------|-------------------|-----------------|
| Central Illinois Public Service | | | |
| Cleveland Electric Illuminating Co. | Avon Lake | Research-Cottrell | |
| Cleveland Electric Illuminating Co. | East Lake | Research-Cottrell | |
| Colorado Ute Electric Assoc. | Hayden | | |
| Columbus & Southern Ohio Electric | Conesville | Research-Cottrell | |
| Detroit Edison | Monroe | Research-Cottrell | |
| Ohio Edison Co. | W. H. Sammis | | Locklin |
| | | | et al. (1980) |
| Pacific Power & Light | Jim Bridger | Flakt/Carborundum | Ashton (1976) |
| Pennsylvania Electric Co. | Keystone | | Katz (1979) |
| Tennessee Valley Authority | Gallatin | | Reese and |
| Tennessee Valley Authority | Widows Creek "B" | | Greco (1968) |
| | | | Dismukes (1975) |
| Texas Utility Generating Co. | Monticello | Research-Cottrell | |
| | | | |

Detroit Edison

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Detroit Edison uses ammonia and sulfur trioxide on Monroe units 1 and 2. The fuel is blended high and low sulfur coals, averaging 2.3% sulfur. Detroit Edison meets the opacity requirements when using the combined conditioning agents. Monroe units 3 and 4 burn the same coal, but their precipitators have 30% higher specific collection area and do not need conditioning.

<u>Ohio Edison</u>

Ohio Edison uses ammonia on their Sammis plant, units 5, 6 and 7. In general ammonia is a useful conditioning agent for low temperature applications (below 150°C) in flue gases from medium sulfur coal.

Pacific Power and Light

Preliminary testing on the Pacific Power & Light, Jim Bridger Plant showed that ammonia conditioning had no effect on the precipitator performance. The fuel is 0.6% sulfur Wyoming coal.

Pennsylvania Electric

Penelec uses ammonia intermittently at Keystone units 1 and 2. They use a medium sulfur coal (1.5 to 2.0% Sulfur). The gas temperature at the precipitator is low (approx. 120°C) and nonuniform. Ammonia is used when the flue gas temperature is very low (winter). With a dosage of 4 to 6 ppmv the efficiency is raised from 96.1% to 99.4% (Katz, 1979). The electrical conditions in the precipitator are improved with ammonia. No sparking is noticed without conditioning; slight sparking is noticed with conditioning. Penelec has problems with dust buildup on the plates and hopper plugging with ammonia conditioning.

Tennessee Valley Authority

TVA has been working with ammonia flue gas conditioning for

twenty years. Reese and Greco (1968) and Dismukes (1976) reported the results of earlier work.

Today the TVA uses ammonia only at Widows Creek "B" unit 7. The fuel is 3 to 3.5% Sulfur coal. The temperature at the precipitator is low (less than 150°C). The precipitator is small (approx. 25 m²/m²/s specific collection area at full load). With 10 to 15 ppm of ammonia conditioning the particle collection efficiency is raised from 70% to 85 or 95%. This still is not high enough to meet compliance requirements. A scrubber has been added to meet the particle regulations and to remove sulfur oxides. The electrostatic precipitator and ammonia conditioning systems are still used to protect the induced draft blowers.

SUMMARY

Effectiveness

The data in Tables 14 and 15 show ammonia conditioning to be effective in increasing the precipitator collection efficiency. This increase in efficiency does not correlate with any change in resistivity of the fly ash.

Unlike sulfur trioxide conditioning, effects of ammonia conditioning occur almost immediately after injection starts. Sulfur trioxide conditioning must penetrate the whole inventory of ash on the collection plates to show any effects, which takes on the order of 8 to 24 hr. Better electrical conditions (higher voltages, lower currents, higher specific power) are noticed immediately on addition of ammonia. Decreased oscillations in the stack opacity are noticed in 30 min to 3 hr.

The magnitudes of the response times indicate the following: 1. The immediacy of the improvement of electrical conditions bears out the space-charge effects discussed by Dismukes (1975) which reduce the voltage drop across the dust layer and increase the voltage drop in the free space.

2. The slower effect on opacity suggests that part of the fly ash inventory on the collection plates is made more adhesive by the ammonia and as a result, reentrainment is reduced.

Ammonia has a low but non-zero electronegativity (White, 1953). Absorption of the free electrons created in the corona zone is improbable, but possible. This absorption of the electrons to form ions of lower mobility may explain the effect of ammonia on precipitator electrical conditions.

The existence of the space-charge effect depends on the presence of efficient charge carriers in the gas. The formation of aerosol ammonium bisulfate fumes (or sulfate, depending on the ammonia-sulfuric acid stoichiometry) creates a large surface area for collection of electrons. These charge carriers will have a lower mobility than electrons (or molecular ions, for that matter). A lower ion mobility allows a more stable corona, higher electrical field strength without breakdown, and larger specific power.

Problems

Plugging of the air preheater is noticed if ammonia is injected upstream of that device. Plugging of the injection nozzles may occur if purge air is not used during shutdowns. Deposits may build up on the discharge electrodes.

Section 5 AMMONIUM COMPOUNDS

Conditioning with ammonium compounds offers a more convenient way of injection of ammonia. The commonly used ammonium compounds are sulfamic acid, ammonium sulfate, and ammonium bisulfate. Once injected, these compounds could decompose to ammonia and sulfuric acid and therefore, may provide a combination of the effects of ammonia and sulfuric acid conditioning.

Many proprietary flue gas conditioning agents contain ammonium compounds. The experience with these agents is also presented in this section.

CHEMICAL PROPERTIES

Sulfamic Acid

Sulfamic acid (NH₂SO₂OH) can be considered the anhydride of ammonium bisulfate, an ammonium-sulfate compound with NH₃ to SO₃ stoichiometry of 1:1. In the crystalline state, it is present as a bipolar ion, ⁺HNH₂SO₃⁻. Its ease of ionization makes it guite soluble in water. Since it is bipolar the molecules are bound tightly in the crystal, making its vapor pressure low. The properties of sulfamic acid are presented in Table 21.

Sulfamic acid decomposes to produce SO, and NH, when injected into the flue gas. Dismukes (1974) reported that above 380°C the sulfamic acid decomposes according to the following equation:

$$NH_2SO_2 OH --> 1/6 SO_3 + 5/6 SO_2 + 1/2 H_2O + 5/60 N_2 + 2/3 NH_3 + 1/6 NO_2$$
(1)

The decomposition rate is slow and therefore long residence time is needed.

At temperatures around 200°C and in the presence of water, sulfamic acid may be hydrolyzed to ammonium bisulfate.

$NH_2SO_2OH + H_2O --> NH_0OSO_2OH$

This would be an effective compound for coating the surface of the particles because ammonium bisulfate is liquid above 144°C to 147°C.

Ammonium sulfate

The solubility, acidity, and decomposition temperature for ammonium sulfate (NH.):SO. are shown in Table 21. The partial pressures of ammonia and sulfuric acid above ammonium sulfate are given in Table 22. The rate of vaporization of ammonium sulfate are shown in Table 23.

Ammonium sulfate is a weak acid in solution, but is highly soluble. As a crystal it has a low vapor pressure. These are similar to the attributes that make sulfuric acid effective. In addition, the presence of ammonia in equilibrium affects the ion mobility in the gas phase and may make the fly ash particles more cohesive.

Ammonium sulfate will decompose to NH, and SO, at elevated temperatures. Spafford et al. (1979, 1980) give the following decomposition reaction for ammonium sulfate at 650°C:

$$(NH_{\star})_{2}SO_{\star} \longrightarrow 2 NH_{3} + H_{2}O + SO_{3}$$
 (3)

On cooling to 160°C Spafford et al. found that liquid ammonium bisulfate was the major recombination product. Further cooling to 90°C produced ammonium sulfate.

Ammonium bisulfate

The properties of ammonium bisulfate are presented in Tables 21 through 23. Like ammonium sulfate, ammonium bisulfate decomposes before it boils at atmospheric pressure. The decomposition products are one mole each of ammonia, sulfur trioxide, and water for one mole of ammonium bisulfate.

(2)

TABLE 21. PROPERTIES OF AMMONIUM SULFATE COMPOUNDS

| | Solubilities | pH at 25°C for | Melting Pt., °C | Decomposition |
|---|-------------------|-------------------|------------------------|---------------|
| | | 0.1 mol/I | · | <u> </u> |
| Sulfamic Acid H₂NSO₂OH | 250 | 1.25 | 205 | 323-467 |
| Ammonium Sulfate (H,NO) ₂ SO ₂ | 790 | 5.5 | 510 (Closed system) | 235 |
| Ammonium bisulfat H₄NOSO₂OH | e 1,000 (25°C) | 1.6 | 144-147 | <200 |

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TABLE 22. EQUILIBRIUM PARTIAL PRESSURES OF AMMONIA AND SULFURIC ACID IN EQUILIBRIUM WITH AMMONIUM SALTS AT VARIOUS TEMPERATURES^a

| Temp, | | (NH ₄) ₂ SC | D. | NH • H SC | | | | |
|-------|--------|------------------------------------|--|----------------------|--|--|--|--|
| °C | [NH]], | atm | [H ₂ SO ₄], atm | [NH ₃] = | [H ₂ SO ₄], atm | | | |
| 120 | 4.40 x | 10 | 2.20 x 10 ⁻ | 1.58 | x 10 ⁻ ' | | | |
| 144 | 3.32 x | 10-, | 1.66 x 10 ⁻⁸ | 1.26 | x 10 ⁻⁶ | | | |
| 175 | 3.28 x | 10-6 | 1.64 x 10 ⁻⁶ | 1.27 | x 10 ⁻⁵ | | | |
| 200 | 1.67 x | 10-5 | 8.36 x 10 ⁻ | 5.33 | x 10 ⁻⁵ | | | |
| 225 | 7.22 x | 10-5 | 3.61 x 10 ⁻⁵ | 2.17 | x 10 ⁻ | | | |
| 300 | 2.72 x | 10-3 | 1.36 x 10 ⁻³ | 6.98 | x 10 ⁻ * | | | |

^a Dismukes, 1974.

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TABLE 23. WEIGHT LOSSES BY VOLATILIZATION OF AMMONIUM SULFATE OR AMMONIUM BISULFATE AT A HEATING RATE OF 4.0°C/MIN^a

| | Temperature, | Cumulative |
|--------------|--------------|----------------|
| Compound | °C | weight loss, % |
| | | |
| (NH) 2 SO) | 200 | 1 |
| | 250 | 2 |
| | 300 | 15 |
| | 350 | 100 |
| | | |
| NH HSO | 200 | 1 |
| | 250 | 3 |
| | 300 | 8 |
| | 3 50 | 25 |
| | 400 | 100 |

a Dismukes, 1974.

Ammonium bisulfate is highly soluble in water and is a good electrolyte. It is a strong acid and is non-volatile. Ammonia bisulfate decomposes easily and exibits many of the effects of both sulfuric acid and ammonia conditioning. It may improve electrical conditions by decreasing ion mobility and decrease rapping losses through greater particle cohesion. It can also decrease the particle resistivity.

CONDITIONING MECHANISM

Ammonium compounds improve ESP performance through one or more of the following mechanisms:

- 1. Decrease resistivity
- 2. Increase space charge
- 3. Increase cohesivity.

Resistivity

Ammonium bisulfate and ammonium sulfate are non-volatile acids like sulfuric acid. They can form layers of conductive solution on the surface of the fly ash collected on the plates and lower the electrical resistivity of the ash layer.

Space charge

The decomposed ammonia and sulfuric acid recombine to form fine particles which accept the electrons from the corona discharge, which form ions of lower mobility. The decreased mobility balances the voltage drop in the interelectrode region between the gas phase and the dust layer. With an adequate electric field in the interelectrode region, the charged particles can migrate faster.

Cohesiveness

The condensation of viscous liquid or the adsorption of reactive compounds on the surface of the fly ash particles increases their affinity for each other on the collecting plates. Greater cohesion between the particles decreases the amount of the particles which become reentrained when the plates are cleaned by rapping.

Conditioning with anhydrous ammonia has been shown to increase fly ash cohesiveness (Dismukes, 1975). It is thought to react with sulfuric acid to form some compound or compounds which bridge the fly ash particles together. Conditioning with ammonium sulfate compounds is expected to do the same.

INJECTION LOCATION

Ammonium compounds in solution can be injected either upstream or downstream of the air preheater.

- Upstream of the air preheater. This position offers a temperature of 600°C or greater and a residence of several seconds.
- Downstream of the air preheater. The temperatures downstream of the air preheater are low, about 120°C to 200°C. Residence time usually is less than 1 second.

In most cases the agents are injected upstream of the air preheater because long residence times and high temperatures are required to vaporize or decompose them. The major disadvantage of injecting at this location is that the air preheater may be plugged and corroded by the reaction products of the conditioning agents.

RESULTS

Results for conditioning wih ammonium compounds are summarized in Table 24. Table 25 shows the results for proprietary chemicals.

Effect on Particle Resistiviy

Dalman and Tidy (1972) and Brown et al. (1978) showed that ammonium sulfate, sulfamic acid, and ammonium bisulfate are effective in reducing the ash resistivity because these compounds can either form a conductive layer of solution on the surface of the particles or decompose to produce SO.. Landham et al. (1981) determined the effects of Apollo LPA-40 and generic ammonium

| Reference | Otility Plant | Fuel Sulfur Wt% | Agent. | Dosage ppmv | Resist- ivity ohm-cm | Specific Coll Area m [#] /(m [#] /s) | Coll, Effi- Ciency | Temper- ature °c |
|-----------|------------------|-----------------------|--------------|---------------------------|----------------------------|--|----------------------------|------------------------|
| Dalmon | Labora- | Low | (NR.),50. | 0 | 7 x 10 ¹ * | | 0.095 ^b | |
| Tiđy | tory | Sulfur | | 55 to 60 ^a | 1 to 2 x 10* | | 0.125 to 0.13 ^b | |
| (1972) | | 011 | ан Ал | 67 ⁸ | 3 x 10° | | 0.14 ^b | |
| | | | | 125 ^a | 3 x 10 ⁹ | | 0.12 ^b | |
| | | | | 140 ^a | 2 to 3 x 10* | | 0.165 ^b | |
| | | | NH.BSO. | 110 ^a | 9 x 10* | | 0.125 ^b | |
| | | | | 127 ^a | 4 x 10* | | 0.135 ^b | |
| | | | NH 2 SO 2 OH | 55 a | 1 x 10" | | 0.142 ^b | |
| | | | | 85 ⁸ | 1.5 x 10" | | 0.142 ^b | |
| | | | | 90 ^a | | | 0.13 ^b | |
| | Station "A" | 1 | Sulfamic | 0 | | | 90 | |
| | Pilot | | Acid | 0.25 ^c to 0.75 | ç | | 96 to 99 | |
| Dismukes | AEPSCo | 0.8 | Sulfamic | 0 | | | 95.3 | 160 |
| (1974) | Appalachian | | Acid | 0.6 ^C | | | 95.1 | |
| | Power | 0.8 | | 0 | | | 78.6 | |
| | Cabin Creek | | | 0.5 ^C | | | 89.7 | |
| | | | | 0.9 ^c | | | 84.6 | |
| | | 1.0 | | 0 | | | 95.3 | |
| | | | | 0.65 ^C | | | 95.1 | |
| | | 1.0 | | 0 | | | 68.9 | |
| | | | | 0.25 ^C | | | 88.2 | |
| | | | | 0.55 ^C | | | 87.6 | |
| | | | | 1.0 ^c | | | 94.0 | |

TABLE 24. ESP PERFORMANCE WITH AMMONIUM-SULFATE COMPOUNDS

a mmol/kg on the ash

b effective migration velocity, m/s

c g/kg coal

| Reference | Dtility Plant | Fuel Sulfur Wt% | Agent | Dosage ppmv | Resist- ivity ohm-cm | Specific Coll Area mª/(mª/g) | Effi- ciency | Temper ature °c |
|-----------|--------------------------------|-----------------------|-----------|-------------------|-----------------------------|------------------------------------|------------------|-----------------------|
| | · | | | | | | | - <u></u> |
| Dismukes | Station "B" | 2.5 | Ammonium | 0. | 10* | | 270 ^d | 150 |
| (1974) | Pilot | | Sulfate | 15 | | | 120 ^d | |
| | Station "C" | 1.0 | Ammonium | 0 | 10. | | 300g | 150 |
| | Pilot | | Sulfate | 15 | | | 160 ^d | |
| | Station "D" | 0.5 | Ammonium | 0 | 1011 | | 58 ^d | 130 |
| | Pilot | | Sulfate | 15 | | | 16 ^d | |
| | Station "B" | 2.5 | Ammonium | 0 | 10' | | 270 ^d | 150 |
| | Pilot | | Bisulfate | 15 | | | 110 ^d | |
| | Unnamed | | Ammonium | 0 | 101. | | | 140 |
| | | | Sulfate | 15 | | | 50 ^e | |
| Brown | Pilot | 0.3 | Sulfamic | 0 | 0.5 to 3 x 10 ¹⁰ | | | |
| et al. | Plant | | Acid | 5 | 101. | | | |
| (1978) | | | | 8 to 10 | l to 8 x 10' | | | |
| | | | | 11 | 1 to 3 x 10* | | | |
| | | | | 65 | 10' | | | |
| | | | | 73 | 10' | | | |
| | | | | 84 | 3 x 10° | | | |
| | | | | 98 | 10 | | | |
| | | | Ammonium | 0 | 3 x 10' | | | |
| | | | Sulfate | 3 to 4 | 0.4 to 1 x 10" | | | |
| | | | | 5 to 10 | 2 to 8 x 10' | | | |
| | | | | 20 to 30 | 7 to 10 x 10* | | | |
| | | | | 91 | 4 x 10* | | | |
| | | | Ammonium | 0.76 ^d | 3 x 10" | | 99.92 | |
| | | | Sulfate | | | | | |

d particle concentration mg/Nm^a

.

e percentage reduction of particle emissions over unconditioned case

| Reference | Utility Plant | Fuel Sulfur Wt% | Dова де ррту | Resist- ivity ohm-cm | Specific Coll Area m'/(m'/s) | Coll, Effi- ciency % | Temper- ature °c |
|-----------|-------------------------------|-----------------------|-------------------|----------------------------|------------------------------------|-------------------------------|------------------------|
| Sparks | Pennsylvania Power 6 light | 1.5 | 0 | 10* | 35 | 97 | 138to 147 |
| (1)/0/ | Montour | | 0.38 ^a | 3 to 5 x 10° | | 99.6 · | |
| Dismukes | New Jerbey | 0.56 | 0 | | | 95 ^b | · |
| (1974) | Gas & Elec | | 0.25 ^c | | | 26 ^b | |
| | Mercer | | 0.38 ^C | | | 3 9 b | |
| | | | 0.5 ^c | | | 22 ^b | |
| | | | 2.0 ^C | | | 22 ^b | |
| | | 1.42 | 0 | | | 27 ^b | |
| | | | 0.6 ^c | | , | 30 ^b | |
| Cragle | Pennsylvania | 2.5 | 0 | | 41 | 43 to 86 ^f | |
| (1976) | Power & Light | 1 | 0 | | | 258 to 387^{f} | |
| | Montour 1 | 1 | 0.4 ^e | | | 172 to 215 ^f | |
| | Montour 2 | 2.4 | 0 | | 41 | 260 ^f | 138 to 154 |
| | | 1.3 | 0 | | | 1200 to 5100 | f |
| | | 1.3 | 1.4 ^e | | | '650 to 860 ^f | |
| McNinch | 5. Carolina | 0.97 | 0 | | | 344 ^{fg} | |
| (1976) | Pub Svc Auth | to | 0.6 | . • | | 155 ^{fg} | |
| | Jefferies 364 | 1.15 | 0.6 | | | 129 ^{fh} | |

TABLE 25. ESP PERPORMANCE WITH PROPRIETARY COMPOUNDS

a cm³/kg coal

b ng/J boiler duty

c g/kg coal

d LPA-40 formulation was mainly sulfamic acid until 1974, then it was changed to ammonium sulfate (Cragle, 1976).

e cm^{*}/kg coal. 1 gal/ton is 4.17 cm^{*}/kg.

f ng/J boiler duty. 1 1bm/MMBTu = 430 ng/J.

9 at reduced load (61% of full).

h at 88% of full load

| TABLE 25. | continued |
|-----------|-----------|
|-----------|-----------|

.____

| Reference | Utility Plant | Fuel Sulfur WtN | Dosage ppnav | Resist- ivity ohm-cm | Specific Coll Area m [#] /(m [*] /s) | Coll, Effi- ciency | Temper- ature °c |
|--------------|------------------|-----------------------|---------------------------------------|----------------------------|--|--------------------------|------------------------|
| Borsheim | Montana | 1.2 | e | · = | | 108 ^{fi} | |
| (1972) | Power | | 0.29 ^e | | | 50 to 80 ^{fj} | |
| | Corvette | | 0.54 ^e | | | 80 ^{f k} | |
| | | | 0.46 | | | 68 to 73^{f1} | |
| Ргеввеу | Arizona | | 0 e | | | 95.2 | 121 |
| et al. | Pub Svc Co | | 0.4 ^e | | | 96.6 | |
| (1979) | Four Corners | • | | | | | |
| Bennett & | #1 | 3.2 to | 0 | | 27.4 | 98.8 | 131 |
| Koker (1978) | | 3.9 | 0.83 ^e | | | 99.5 | |
| | 12 | 0.5 | 0 | | 69 | 22 to 30 ^m | 365 |
| | | | 0.29 | | | 12 ^m | |
| | #3 | 0.8 to | 0 | | 34 | 161 ^f | 127 |
| | | 1.5 | 0.63° | | | 116 ^f | |
| | | | 0.63 ^d & 0.42 ^e | | | 45 ^f | |
| | 14 | 1.3 to | 0 | | 34 | 925 ^f | 133 |
| | | 1.7 | 0.31 ^e & 0.42 ^e | | | 39f | |
| Bennett & | | 0.6 | 0 | | 37 | 293 d | 168 |
| Toher | #5 | to | 0.21 ^e | | | 176 ^d | |
| (1978) | | 1.0 | 0.42 ^e | | | 155 ^d | |
| | | | 0.42 ^e 6 0.42 ^e | | | 86 d | |

e cm³/kg coal

í.

ng/J boiler duty ſ

1 at 148 MW load

1 at 158 MW load

k at 163 MW load

1

at 173 MW load opacity, percent m

| | | | | | | Coll, | |
|--------------------|------------------|-------------|---------------------------------------|---------|-------------|--------|-----------|
| | | Puel | | Resist- | Specific | Effi- | Temper- |
| | Utility | Sulfur | Do sa ge | ivity | Coll Area | ciency | ature |
| Reference | Plant | WES | ppmv | ohm-cm | m */(m */s) | • | •c |
| Landham | Montana | 0.7 | 0 | 3 x 10• | 28 | 77.3 | 130 |
| et al. | PWE | | | | | | |
| (1981) | Corvette | 0.7-1.0 | 0.4 ^d | 10• | | 97.5 | |
| | Tampa | 1.1-1.2 | 0 | 2 x 10" | 65 to 68 | 99.90 | 160 |
| | Elect. | | | | | | to |
| | Gannon | | 0.660 | 3 x 10° | | | 170 |
| | | | 0.29 ^d | 3 x 10• | | 99.96 | |
| Patterson | Unnamed | 0.9-1.6.2.6 | 0 | | 32 to 35 | 99.7 | 107 to |
| et al. (1979 b) | | | 0.42 ^d 6 0.31 ^d | | | 99.9 | 117, 141 |
| | • | | | | | | |
| Patterson | Tampa | 1.0 to 1.2 | 0 | | | 98.9 | 147to 165 |
| et al. (1981) | Elect. Gannon | | 0.63 ^d | | | 99.5 | |

TABLE 25. Continued

sulfate on ash resistivity in full scale installations and found both reduce resistivity (Table 25).

Pressey et al. (1979) and Patterson et al. (1979b) reported the field test results of Apollo LPA-455, which is a solution of diammonium hydrogen phosphate. They found that LPA-445 has no effect on particle resistivity.

It seems that in most cases ammonium compounds can lower the ash resistivity. However, it is not as effective as SO₂. With ammonium compounds, the resistivity decreases by about half an order of magnitude.

Cohesiveness

Ash cohesiveness is usually indirectly measured by the magnitude of the opacity decrease during rapping. An opacity trace with smaller periodic spikes can be attributed to decreased reentrainment due to rapping.

Patterson et al. (1979b) show an opacity meter trace for a plant using Apollo LPA-445 conditioning. The baseline (no conditioning) opacity was 15-18%. The spikes corresponding to rapping ranged from 40% to greater than 60% opacity. With LPA-445 conditioning the inter-rapping opacity was 12 to 13% and the peaks of the rapping spikes were between 14 and 21% opacity. Therefore LPA-445 is effective in increasing ash cohesiveness. This could be due to the phosphates in the agent which form polymers on decomposition. The coprecipitation of these polymers or the coating of the fly ash surface with the polymers could increase the cohesivity.

No information was reported for the other ammonium compounds.

Space Charge

Pressey et al. (1979) performed a simultaneous impactor, optical, and condensation nucleus sampling at the Four Corners station of the Arizona Public Service which used Apollo LPA-445 conditioning agent. They found a significant increase in the numbers of fine particles. The condensation nucleus count was

10¹⁰ to 10¹¹ m-³ with conditioning versus 10⁰ m-³ without. The optical particle measurements showed a shift in size from small particles (0.3 - 2 μ m) to larger ones (2-3 μ m) when conditioning was shut off.

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Emissions Caused by the Agents

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Table 26 shows the partition of injected ammonium compound as reported by Landham et al. (1981). The data were collected in Gannon Station of Tampa Electric. It appears that the ammonium sulfate is distributed between the gas phase and particulate phase entering the ESP. Most of the ammonia produced is collected in the ESP.

Patterson et al. (1981) reported sampling results at the same plant. They reported an increase in the particulate sulfate and iron compound emissions with Apollo LPA-40 conditioning agent. The particulate sulfate emission was about 20 μ g/m³ and 1,500 μ g/m³ for unconditioned and conditioned operation. The sulfate particles were emitted mostly in the submicron size range.

Ammonium phosphates are known to decompose to ammonia and either phosphorus pentoxide or to various condensed polymeric forms of phosphate. Spafford et al. (1979) found that Apollo LPA-445 decomposed mainly to gaseous ammonia and condensed phosphates. Some unreacted orthophosphate ion was also detected.

The major recombinations products at 160°C and 90°C were distributed among ammonium phosphate, sulfate and nitrate salts. Phosphine (PH₃), a toxic gas, was not found to be a reaction product.

Problems

The most common operating problem with ammonium compound conditioning agents has been plugging of the air preheater by deposits of condensation products when the agent is injected upstream of the air preheater.

| Reference | Temp °C | Injected NH, | ppmv SO, | Location at ESP | Gae NH, | Phase SOı | Partic NH, | le Phase SO, | Conditioning Agent |
|----------------------|------------|-----------------|-------------|--------------------|------------|--------------|---------------|-----------------|----------------------------------|
| Landham et al. | 165 | 12.2 | 6.1 | Inlet | 3.6 | 2.4 | 4.5 | 2.8 | LPA - 40 injected at 540°C |
| 1981 (Gannon) | | | | Outlet | 0.2 | 0.9 | 0.2 | <1 | |
| | 165 | 12.8 | 6.4 | Inlet | 2.2 | 1.2 | 2.2 | 6.6 | LPA - 40 injected at at 179°C |
| | | | | Outlet | 0.2 | 1.9 | 0.1 | <1.7 | |
| | 165 | 10.6 | 5.3 | Inlet | 2.6 | 0.8 | 7.3 | 2.9 | (NH.),SO. injected at 175°C |
| | | | | Outlet | 0.3 | 0.6 | 0.1 | <1 | |
| Landham et al. | 133 | 6.8 | 3.4 | Inlet | 2.6 | <0.5 | 0.73 | 12 | |
| (1981) (Corrette) | | | | Outlet | - | - | 0.21 | - | |
| | | 7.4 | 3.7 | Inlet | 2.4 | 0.75 | 0.33 | 12 | |

TABLE 26. FATE OF AMMONIUM COMPOUND CONDITIONING AGENTS

Outlet - 0.7 0.02 0.95

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ECONOMICS

No information on capital investment is available. Landham et al. (1981) reported the following operating cost for conditioning with Apollo LPA-40:

Montana Power \$0.042 mills/kwH (Corrette) (1981) Tampa Electric \$0.024 mills/kwH (Gannon) (1982) Patterson et al. (1979b) showed costs for Apollo LAC-51B and LPA-445.

| LAC | 51B | \$0.052 | mills/kwH | (1982) |
|-----|-----|---------|-----------|--------|
| LPA | 445 | \$0.031 | mills/kwH | |

USER EXPERIENCE

Table 27 shows a list of past and present users of ammonium compounds and proprietary chemicals. No user experience was reported.

Because of air preheater plugging problems, the following utility companies have discontinued the use or testing of these chemicals.

Colorado Ute Electric Association - Hayden Northern Indiana Public Service - Mitchell Florida Power - Crystal River Pennsylvania Power and Light - Montour

TABLE 27. LIST OF PAST AND PRESENT USERS OF AMMONIUM COMPOUND AND PROPRIETARY CHEMICALS

| <u>Company</u> Name | <u>Plant Name</u> | Licensor | References | | |
|---|-------------------|---------------|-----------------------|--|--|
| Arizona Public Service Co. | Four Corners | Apollo | Pressey et al. (1979) | | |
| Baltimore Gas & Electric | H. A. Wagner | Apollo | Locklin et al. (1977) | | |
| Central Illinois Light | Duck Creek | Apollo | | | |
| Colorado Ute Electric Assoc. | Hayden | Apollo | | | |
| Florida Power | Crystal River | Apollo | | | |
| Georgia Power | Harllee Branch | Apollo | | | |
| Montana Power Co. | J. E. Corette | Apollo, Nalco | Borsheim (1977) | | |
| New England Power Co. | Brayton Point | Nalco | | | |
| New England Power Co. | Salem Harbor | Nalco | Locklin et al. (1980) | | |
| New York State Electric & Gas | Goudey | Apollo | | | |
| Northern Indiana Public Service Co. | D. H. Mitchell | Apollo | | | |
| Ohio Edison Co. | Edgewater | Dusco | | | |
| Ohio Edison Co. | Gorge | Dusco | | | |
| Ohio Edison Co. | W. H. Sammis | Apollo | | | |
| Pacific Power & Light | Centralia | | | | |
| Pennsylvania Power & Light Co. | Montour | | Locklin et al. (1980) | | |
| Pennsylvania Power & Light Co. | Brunner Island | | Locklin et al. (1980) | | |
| Public Service Co. of Colorado | Valmont | Nalco | | | |
| Public Service Electric & Gas, New Jersey | Hudson | Apollo | | | |
| Public Service Electric & Gas, New Jersey | Mercer | Apollo | | | |
| South Carolina Public Service Authority | Jefferies | Apollo | McNinch (1976) | | |
| Tampa Electric Co. | Big Bend | | Locklin et al. (1980) | | |
| Tampa Electric Co. | F. J. Gannon | Apollo | | | |
| Texas Utility Generating Co. | Big Brown | Apollo | McGraw (1980) | | |
| Toledo Edison | Bayshore | Nalco | Locklin et al. (1980) | | |
| Virginia Electric & Power | Yorktown | Apollo | Locklin et al. (1980) | | |

Section 6 ORGANIC AMINES

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CHEMICAL PROPERTIES

Organic amines, such as triethylamine and cyclohexylamine, have been studied in the laboratory and pilot scale ESP's as possible flue gas conditioning agents by researchers in Australia and the United States, e.g. Potter and Paulson (1974), Collin (1978), and Bickelhaupt et al. (1978). Currently there are no industrial users.

Of all the amines, triethylamine, $(C_2H_3)_2N$, has received the most attention. It is an organic nitrogen compound and is highly soluble in water. It behaves similar to ammonia, but is a substantially stronger base than ammonia. The melting point and boiling point of triethylamine is -115°C and 90°C, respectively. It decomposes extensively to ammonia, hydrogen cyanide, nitrogen dioxide, and nitric oxide at temperatures above 345°C (650°F) (Spafford et al., 1979).

Conditioning Mechanism

The mechanism of triethylamine conditioning is not fully understood. Potter and Paulson (1974) mentioned that triethylamine increases particle size by agglomeration of suspended particles. This is a speculative statement based on measured ESP performance rather than on actual size distribution measurements.

Based on available data, it seems that triethylamine improves the voltage-current characteristics by means of reducing the ash resistivity. Triethylamine is adsorbed on the surface of fly ash and forms a conductive layer (Bickelhaupt et al., 1978; Collin, 1978).

Injection Location

Since there are no industrial users of triethylamine, no preferred injection location has been established. Spafford et al. (1979) recommended, based on results from the thermal

decomposition experiments, that the gas temperature at the injection point be below 370°C. Bickelhaupt et al. (1978) found that the effectiveness of triethylamine increases with decreasing gas temperature. Therefore, it seems that the logical injection location is after the air pre-heater.

Even though triethylamine is less volatile than ammonia, it can be injected in the vapor phase as well as in solution form. Dosage ranges from 20 to 140 ppm.

RESULTS

Effects on Particle Resistivity

Brown et al. (1978) measured in-situ the ash resistivity with a point-to-plane probe in the flue gas from a pilot-scale boiler which burned western Alberta bituminous coal with 0.3% sulfur, 13% ash, and over 30% low reactivity macerals. They found that triethylamine is effective in reducing the ash resistivity. The resistivity decreased from 3 x 10° ohm-m without conditioning to 5 x 10° ohm-m with a triethylamine dosage of 60 ppm (Figure 2).

The results of a laboratory study by Bickelhaupt et al. (1978) showed similar conclusions. With an injected concentration of 25 ppm of triethylamine, the resistivity decreased one to two orders of magnitude in the temperature range of 102°C to 150°C for specific ashes. It is more effective with lower temperatures, less basic ash composition, and greater concentration of the agent.

Emissions Caused by the Agent

Because there are no industrial users, emissions caused by organic amine conditioning have not been determined.

Spafford et al. (1979) analyzed the thermal decomposition products of triethylamine. They found the compound decomposes extensively at 650°C, but remains largely intact molecularly at lower than 370°C. It is capable of reacting with either sulfur dioxide or sulfuric acid to form bisulfite, sulfite, bisulfate,



Figure 2. Ash resistivity versus triethylamine concentration (Brown et al., 1978)

or sulfate salt. One of the detected decomposition products is the carcinogen, N-nitrosodiethylamine.

BCONOMIC AND USER EXPERIENCE

Triethylamine has only been studied in the laboratory and in pilot plants. There are no industrial users. Therefore, no economic data and user experience are available.

Section 7 ALKALI CONDITIONING

The combustion of many Western coals produce high resistivity ash which is difficult to collect. Analysis of the ash revealed that the ash is low in alkali. Bickelhaupt (1974) found the resistivity of fly ash is inversely proportional to the amount of sodium and lithium present in the ash. Therefore, attempts have been made to decrease the ash resistivity by increasing the alkali concentration in the ash.

Of the many alkali compounds, sodium salts are the most commonly used conditioning agents because of their availability and relatively low cost. The widely used sodium compounds are sodium carbonate and sodium sulfate. Sodium chloride has been tried in the laboratory and found to be effective. However, it is not used because it can lead to metal corrosion.

Alkali earth compounds, including dry limestone and magnesia have also been studied. These compounds react with excess sulfuric acid to enhance the space charge effect.

CONDITIONING MECHANISM

If the sodium compound is co-precipitated with the ash, the compound trapped in the space between the particles on the dust layer offers an additional conductive path for charge dissipation.

If the sodium compound is injected in the boiler along with coal, sodium is bound in ash and it affects resistivity the same way as natural sodium (Gooch et al., 1982).

INJECTION LOCATION

Sodium conditioning, unlike the other conditioning agents, is not limited to cold side ESP's. It can be added to the boiler along with the coal or into the flue gas just ahead of the ESP. In the first case, sodium oxide from the injected compound is incorporated in the ash as a resistivity-lowering constituent. When added to the flue gas, it is co-precipitated with the ash, serving as a conductive species in a mixture with the relatively nonconductive fly ash.

The sodium compound can be applied either in solution form or in dry powder form. No matter where and how sodium conditioning is applied, the most important parameter which affects its effectiveness is mixing of sodium salt and fly ash. To be effective, the sodium must either be incorporated into all the ash particles or co-precipitated with the ash on the plates yielding well mixed deposits.

When the sodium is applied in dry powder form for coprecipitation, there may be difficulties in obtaining well mixed deposits as have been discovered by Gooch et al. (1980, 1982). Lederman et al. (1979) applied sodium in solution form to a hot-side ESP and claimed that uniform coating of sodium salts on ash particles was obtained.

Gooch et al. (1981) added sodium compound to the coal supply prior to pulverization as a means of supplementing the sodium content of the fly ash. They speculated that complete decomposition and volatilization of the conditioning agent occurred in the boiler and subsequent condensation of the sodium compound should be uniformly distributed and become an integral part of the fly ash surface.

As a coal additive, the dosage is such that the resulting alkali concentration (expressed as Na_2O) is about 1 to 2% by weight. When the agent is injected for co-precipitation with the ash, the dosage is 2 to 5% of solids as Na_2O . The coprecipitated sodium compound should have a particle size distribution comparable to that for the ash.

RESULTS

<u>Bffects on Particle Resistivity</u>

Sodium is effective in reducing the fly ash resistivity if the sodium is mixed well with the ash. Schliesser (1981) demonstrated the effectiveness of sodium carbonate dry powder as a conditioning agent on a pilot precipitator cleaning and the cold-side slipstream from a commercial boiler. In situ

resistivity measurements have shown a decrease in resistivity from 2.1 x 10^{10} Ohm-m without conditioning to 3.7 x 10° Ohm-m with a 1.0 to 1.5% concentration of sodium carbonate as sodium oxide.

Gooch et al. (1980) reported pilot field test results on the co-precipitation of sodium carbonate powder with high resistivity fly ash in a cold-side ESP. In situ resistivity of the ash was reduced from 1×10^{10} to 1×10^{0} Ohm-m when the sodium oxide content of the ash was increased to 2.5% from the original 0.3%.

However, in a later report on the same study Gooch et al. (1982) concluded that coprecipitation of fly ash and injected dry sodium carbonate powder in a cold-side ESP is ineffective in lowering the resistivity. The powder was injected at 160°C and the mass median diameter of the powder was 30 μ m. Gooch et al. (1982) speculated that the following two factors may be responsible for the ineffectiveness of cold-side conditioning with dry sodium carbonate powder:

- The presence on the plates of a residual layer of high resistivity ash that can not be removed by rapping or washing.
- The ash and sodium carbonate deposit on the plate is inhomogeneous.

Precipitator Performance

Table 28 and Figure 3 shows the reported ESP performance with and without sodium conditioning. Based on these data, sodium conditioning is effective in improving the ESP performance when a uniform distribution of sodium compound is obtained. The improvement in ESP colleciton efficiency is less with coprecipitation of Na₂O₂ than with SO₂ conditioning.

Problems

Industrial users only have a limited experience with sodium conditioning and operational problems are not well documented.

TABLE 28. ESP PERFORMANCE WITH SODIUM SALT CONDITIONING

| Utility Plant | Fuel Sulfur, wt% | Agent | Dosage | remperature | Specific Coll. Area m² <u>/(m³/s)</u> | Collection Efficiency, | Reference |
|---|------------------------|---------------------------------------|---|--------------|---|---------------------------|-------------------------------|
| Wisconsin Power | - | 15% Na 2003 | 0 | 370 to 400°C | - | 84 | Lederman, et al. |
| Columbia Station | | | 2 to 5% of sodium as Na₂O in solid | 5 | | 99.3 | (1979) |
| Public Service Co. of Colorado - Comanche Station Unit #2 | - | 15% Na₂CO₃ Solution | 0 2 to 5% wt. of sodium as Na₂O in solid | 370°C s | - | 98.0 99.8 | Lederman, et al. (1979) |
| City of Colorado Springs, Colorado Martin Drake Power Plant, Unit #5 | - - | Na 200 3 | 0.5 to 3.5% Na₂O in ash | 160°C | 77.2 | - | Gooch et al. (1980) |
| Gulf Power Company Lansing Smith Plan Units #1 and #2 | t | Sodium Sulfate Added to coal | 0 0.96% Na2O in ash; (2.1 kg Na2SO 100 kg coal) 1.9% Na2O in | 350°C | 63.8 | 98.21 99.64 99.71 | Gooch et al. (1981) |
| City of Colorado Springs, Colorado Martin Drake | - | Na ₂ CO ₃ | 0 1.5 to 3.5% Naz in ash | 160°C | 65 65.1 | 87.5 92.3 to 93.5 | Gooch et al. (1982) |

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PARTICLE DIAMETER, MICROMETERS

Figure 3.

. Fractional efficiency for three performance tests. (Gooch et al., 1981)

However, there is one potential problem associated with the addition of sodium compound to the coal. The sodium may cause ash slagging and boiler fouling if the system is not operated properly.

ECONOMICS

Lederman et al. (1979) provided investment data for a liquid solution conditioning system. The capital costs are about \$1.55 to 3.00 per installed kW. The operating costs, excluding depreciation, is about 0.03 mills/kWh.

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