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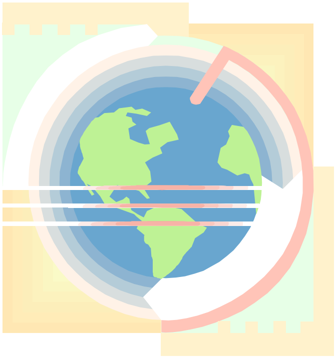
AMMONIA CONDITIONING OF FLUE GASES



A White Paper

ABSTRACT

Numerous investigators reported use of the ammonia conditioning with various degrees of success. Ammonia conditioning usually works best with the acidic fly ash. If injected ahead of the air heater tendency to plug (unless air heater temperatures were unusually high - >400^{E}F) the air heater was reported as an additional, but unwanted result. Ammonia injection downstream of the air heater was reported to be unpredictable.

No effect of the ammonia on the fly ash resistivity was reported with any degree of certainty. Instead, the effect of ammonia appeared to be an enhancement of the space-charge component of the electric field. In addition, increase of the cohesiveness of collected ash and a reduction of the re-entrainment appears to be another "major player" in successful application of the ammonia conditioning.

This paper presents results of the literature review to identify the "what's..." and "why's..." of the ammonia conditioning. It will attempt to focus on a mechanism of the ammonia conditioning and specifics of its successful or unsuccessful applications. The presence of trace amounts of the alkali materials may contribute appreciably to the conductivity of the fly ash particles.

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INTRODUCTION

Electrostatic precipitation is a process using electric forces to separate suspended particles form gases. Fortunately, the precipitation process can be effectively carried out over a wide range of dust and gas properties and conditions. In cases where precipitation is difficult, steps are usually taken to improve the dust or gas properties and thereby increase the precipitability of the dust. The most known and widely used technique is to add trace amounts of a "conditioner", which when mixed with the gas and dust under the right conditions, alters their properties so as to move them into a range of good precipitation.

Because this is and electric process, the electrical conductivity of the material being collected is of paramount importance. Highly conductive dusts with resistivity of less than 10^4 ohm-cm can be charged and collected very easily. However, because they are so conductive they bled of their charge to the grounded collection plate rapidly and are prone to escape the collection zone, either because of electrical repulsion back into the gas stream, or because of simple re-entrainment be the passing gas. Highly resistive dusts with resistivity over 10^{11} ohm-cm exhibit opposite phenomena. Once collected on the collecting plates, the collected dust layer will be tightly held in place by a corona current, however, because the high resistivity dust the voltage drop can build up to such levels as to cause the well known back corona phenomenon, which in its most severe form can reduce precipitator collecting efficiency to nearly zero.

By far the largest body of work in the art of the fly gas conditioning ash been devoted to attempts to lower the dust resistivity. Conditioning is as old as the art of precipitation itself. As early as 1912 it was discovered that copper converter dust precipitation was considerably enhanced by the presence of sulfur trioxide or increased moisture of exhaust gases.

Progress in the application of conditioning agents for precipitator performance enhancement has been erratic. In the petroleum industry ammonia conditioning of catalyst cracker gases has been accepted for many years. Conditioning of utility boiler flue gases has been proven over and over and is a widely accepted technology today. It has been proven now that chemical conditioning affords an alternative to increased precipitator size as a solution to fly ash collection form boilers burning low sulfur coals.

I. AMMONIA FLUE GAS CONDITIONING

The value of ammonia as a conditioning agent was reportedly discovered in 1942 in efforts to deal with high resistivity of catalyst dust in the petroleum industry. The use of the ammonia for treating fly ash in coal-fired power plants, on the other hand, is "comparatively" new. First reports of the *intermittently* successful use of the ammonia as a conditioning agent were reported in Australia by Watson and Blecher in 1966. The results of this study showed good results while using the ammonia as a conditioning agent. There the SO_3 flue gas conditioning was proved to be ineffective due to the highly acidic ash (pH of 3.5-4) and, thus, speculations were that conditioning with a basic rather than acidic agent might prove more effective. The initial pilot plant trials with ammonia conditioning conducted at the Tallawarra plant in 1959 found to be very successful. Similar promising results were obtained at the No. 5 Tallawarra precipitator. However, subsequent ammonia conditioning at the No. 6 precipitator at the Tallawarra did not produce the same encouraging results that were obtained on No. 5.

The electrical behavior of the precipitators with ammonia conditioning changed considerable within minutes after the introduction of ammonia into the flue gas. Increases of 50 to 100% in electrode potential and corresponding decreases in electrode current were maintained consistently and tent to persist for several hours after ammonia injection is stopped.

Further resistivity measurements were carried out, however, these presented rather perplexing results when ammonia-conditioned dust was evaluated. It is generally accepted that the increase in precipitation efficiency brought about by flue gas conditioning is caused be a reduction in the particle surface resistivity and the elimination of back corona, a phenomenon reported to be quite common with new South Wales fly ash. The resistivity of the ammonia-conditioned ash, however, showed no appreciable difference from that of non-conditioned fly ash. Both were in the range of 10^{13} to 10^{14} ohm-cm, which is certainly well above the critical level of 10^{10} ohm-cm suggested by Dr. White.

Watson and Blecher then went on with a hypothesis that, perhaps ammonia gas conditioning changed flue gas characteristics sufficiently to eliminate back corona and/or the forces of particle adhesion and cohesion sufficiently to bring about cleaner electrodes and, hence, better performance.

Shortly thereafter Baxter reported success with ammonia conditioning several plants in the United States, where apparent effect was to lower ash resistivity in some instances and to increase it in the other instances. Initially, he injected sulfur trioxide with the unsatisfactory results. Performance improvement was attained only by the use of excessive conditioning which allowed an objectionable acid vapor plume to escape the stack. The presence of the acid plume indicates that the necessary adsorption on the dust particles was not occurring. Where sulfur trioxide conditioning has been effective, stack measurements show no increase in effluent SO_3 concentration, rather the injected gaseous agent attaches to and is discharged with the dust collected in the precipitator as reported by Durby and Hendrich. Analyses of the collected ash indicated that SO_3 flue gas conditioning reduced laboratory measured resistivity form 10^{12} to 10^{11} ohm-cm and increased acidity of the dust from a pH of 5.5 to 3.5.

Subsequent trials with ammonia injection reportedly produced marked precipitator performance improvement. Dust analyses showed decrease in resistivity similar to that mentioned with sulfur trioxide conditioning, however, the pH of the ash increased to a neutral condition. Although he reported varying success with precipitator performance, improvement has been accompanied by air heater plugguage at each test location.

Finally, the tests reported at the power plant with two identical cyclone fired boilers produced still unexplained results, i.e. units reacted in very explicitly different manner. One of the units responded well to the ammonia injection, while the other reacted rather poorly. Moreover, chemical and physical analyses of the dust produced no reasons for such a difference. The resistivity was measured and actually increased. Dust ph also increased but remained quite acidic. Unfortunately authors did not publish detailed coal and analyses. Furthermore, it is worth noted that, according to the author, "No correlation can be established between effectiveness and initial ash resistivity, nor between ammonia injection and treated ash resistivity".

In 1968, Reese and Greco were successful in the use of ammonia to treat the fly ash from high sulfur coal (they concluded that the effect of ammonia was to overcome an unfavorably low resistivity stemming from an excess of naturally occurring sulfur trioxide).

Some of the trials with ammonia flue gas conditioning have been successful, but others have not produced the desired results. One source of difficulty in the use of the ammonia conditioning has been the absence of basic information on mechanisms of conditioning be this compound and the circumstances in the power plant to favor its use.

II. CHEMICAL REACTIONS INVOLVED WITH AMMONIA CONDITIONING

Elementary explanations of ammonia conditioning effects have assumed that the chemical compounds formed when ammonia is injected, either concurrently with injection of sulfur trioxide or when the latter is formed by "natural" (combustion) processes in sufficient quantities, are only ammonium bisulfate NH_4HSO_4 or, if the stoichiometric ratio is appropriate, the normal sulfate $(NH_4)_2SO_4$. Besides these, the existence of intermediate chemical compounds is possible. The melting points change continuously according to the H_2SO_4/NH_3 stoichiometric ratio, and there is a possibility that compounds with very low melting points may be formed in the process. In addition, the ones which are stable in solid form at temperatures above 150 ^{o}C (300 ^{o}F) are those with stoichiometric ratios 1.2 and above.

Ammonia flue gas conditioning is very little understood, especially as to the mechanism involved in improving ash resistivity. The chemical reaction postulated by Rendle and Wildson teaches that ammonia will react with any natural sulfur trioxide present and moisture to produce ammonium bi-sulfate:

$$SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_4$$

In the presence of excess ammonia this reaction will slowly continue to produce ammonium sulfate:

$$NH_4HSO_4 + NH_3 \_ (NH_4)_2SO_4$$

Lacking excess ammonia or as cooling occurs the liquid bi-sulfate will freeze at temperatures below 297 ºF into a sticky solid. It is this adherent nature of the resultant that has been a "suspect" to play a major role in the precipitator performance improvement.

III. MECHANISMS OF THE AMMONIA CONDITIONING

III.1 EFFECTS OF AMMONIA ON THE ELECTRICAL RESISTIVITY

The use of ammonia (NH_3) for modification of dust resistivity has not been developed to the same degree as SO_3. Some experiments have shown that ammonia injection improved the collection of fly ash in ESP's, but it is not clear whether the improvement resulted from resistivity modification or other effects. Other trials have shown little or no change in fly ash resistivity or ESP performance.

There has been much debate by many authors regarding the use of ammonia alone for modifying the electrical resistivity of fly ash. One argument suggests that for high resistivity ashes a reduction in resistivity might be produced, permitting higher voltages and currents to be maintained without sparking or back corona. On the other hand, for lower resistivity ash an increase in resistivity due to neutralization of excess acid might permit a sufficient electric field to exist in the ash on the precipitator collection electrodes to overcome losses from rapping reentrainment.

While successes have been reported using ammonia as the sole conditioning agent for some low sulfur Australian coals, U. S. experience has been improved precipitator performance for some low sulfur coals and not for the others. It has been theorized that ammonia conditioning is more effective for acidic ashes in terms of the relative concentrations of acidic and basic oxides present (acid/base ratio) but this has not been true in every case.

Ashes having high acid/base ratios with small to moderate amounts of sulfur trioxide present in the flue gas can have high resistivity and it may be that resistivity is reduced as a result of ammonium bisulfate acting to facilitate sulfur trioxide attachment. If little or no sulfur trioxide were present, ammonia alone might have little effect. This hypothesis is somewhat speculative at present in view of the small number of observations documented.

A study of the effects of the ammonia on the electrical resistivity of the silica-alumina catalysts may shed some light on the possible mechanism of the conductivity improvement on one hand and, perhaps, answer numerous questions why ammonia is very unpredictable in its conditioning nature.

It has been demonstrated that sodium and potassium increase the conductivity of silica-alumina materials (note: fly ash is predominantly silica-alumina compound) at about 400 ºF or higher. It was further speculated that the increased conductivity results from ionic conduction of sodium and potassium ions. Ammonia and amines are reported to markedly increase the resistivity of silica-alumina catalysts below 200 ºF. The increased conductivity is closely associated with large amounts of physical adsorption, which probably increases the mobilities of the current carriers. The irreversible adsorption of ammonia below 200 ºF is independent of temperature and is measure of the acid sites on the particulate. The reversible adsorption increases with decreasing temperatures. The increase in conductivity depends on the properties of both adsorbate and the particulate.

The chemisorption of ammonia on silica-alumina compounds like fly ash particles results in the formation of ammonium ions from reaction of ammonia with protons on the ash particles surface. This, perhaps, could be responsible for the power resistivity over the temperature range of 300-500 ºF. In ammonia it seems reasonable to conclude that most of conductivity occurs on the surface. The physically adsorbed ammonia offers an excellent medium for the passage of ions. In addition, the relative size of the ammonia ion, the internal structure of silica-alumina and the temperature regions where the precipitators are operating are not favorable for ionic conduction (by ammonium ions) in the bulk. The exact mechanism of the increased surface conductivity resulting form ammonia adsorption is difficult to deduce but one could speculate that presence of traces of alkali metals would contribute appreciable to the conductivity of the fly ash particles.

III.2 IV.2 PRECIPITATOR PERFORMANCE IMPROVEMENT

Ammonia in the presence of sulfur trioxide may work in a variety of ways. Although the exact mechanisms responsible for improved precipitator performance are not completely defined, they appear to include such phenomena as an improved acid attachment, space-charge effects, agglomeration and increased cohesiveness of the fly ash.

III.2.1 Sulfuric Acid Attachment

Some evidence suggests that injection of ammonia promotes improved attachment of available sulfuric acid to fly ash particles, making it more effective for resistivity control. It creates a thin conductive film on the ash surface believed to consist of low melting point ammonium sulfate products, which contributes to resistivity modification. It has been suggested that the addition of ammonia improves upon the efficiency of the sulfur trioxide conditioning by an additional charge carrier, the NH_4^+ ions.

In some low sulfur coals the percentage of acidic compounds in the ash (aluminum oxide, iron oxide, and silicon oxide) is high (above about 90 percent). Here, the injection of sulfur trioxide alone to reduce resistivity loses some of its effectiveness because the acidic sulfur trioxide cannot readily attach to the highly acidic ash at higher temperatures. Substantial amounts of excess sulfur trioxide must be injected while treating such ashes to produce a conductive film on the surface.

Since the conditioning process is concerned with application of an acid film to the surface of the fly ash particles, it is clear that the coal ash content will affect the amount of acid to be injected. Acquisition of an acid film by the fly ash particles is presumed to take place by a condensation/partial pressure deposition process and would therefore be expected to be temperature sensitive.

Dr. Frisch has shown that the surface composition of the ash particles can affect acid attachment [17]. Dr. Bickelhaupt also showed that a "threshold" effect was exhibited by certain ashes, evidenced by a lack of change in resistivity at ambient acid concentrations below the threshold level [18]. These phenomena are clearly related to ash chemistry, and call for inclusion of all possible combinations of ash chemical properties as variables to be tested for significance.

Those who have studied factors affecting the resistivity of fly ash in a flue gas atmosphere are very familiar with the hump-backed characteristic of resistivity as a function of temperature. Generally, resistivity has a maximum value at a temperature around 300 ^{o}F with decreasing values above and below the maximum point. In determining the amount of SO_3 to be required to reduce the ash resistivity to a desired lower value, one would think that the maximum rate would be required at the maximum unconditioned resistivity point, with decreasing amounts at higher and lower temperatures. That is, a hump-backed curve of injection rate reflecting the unconditioned resistivity characteristic would be expected. An interesting discovery made in the development of SO_3 flue gas conditioning is that the amount of SO_3 required to attain a desired level of resistivity follows the expected dome-shaped curve with respect to temperature only up to a point, after which it breaks off to a rapidly rising characteristic [19].

The inflection point between the two portions of the curve is a function of the surface chemistry of the ash, occurring at relatively low temperatures for acidic ashes and at higher temperatures for basic ashes. The range of variation of the inflection point temperature appears to be approximately from 250 ^{o}F to 400 ^{o}F for coals available worldwide. If the flue gas temperature is above the inflection point, the portion of the injected SO_3, which is greater than the level of the dome-shaped portion of the curve, does not attach to the ash and will be passed through the ESP. In the rare cases where a wet scrubbing system follows the ESP the excess SO_3 will be captured; otherwise an objectionable blue plume will be formed if the emitted SO_3 concentration approaches 10 ppmV or more.

The inflection point effect explains some of the difficulties various experimenters have encountered in attempting adjustment of ash resistivity with sulphur trioxide alone. In some low sulfur coals the percentage of acidic compounds in the ash (aluminum oxide, iron oxide, and silicon oxide) is high (above about 90 percent). Here, the injection of sulfur trioxide alone to reduce resistivity loses some of its effectiveness because the acidic sulfur trioxide cannot readily attach to the highly acidic ash at higher temperatures. Substantial amounts of excess sulfur trioxide must be injected while treating such ashes to produce a conductive film on the surface. Furthermore, if the operating temperature is much higher than the inflection point, no reasonable amount of injected SO_3 will be effective in reducing the resistivity.

The temperature at which inflection occurs is a function of ash surface conditions, i.e. a measure of susceptibility to attachment of acid. The increased requirement for sulfur trioxide at temperature above the inflection point indicates the required partial pressure of sulfur trioxide needed to attach sufficient sulfuric acid to the particles to obtain the desired ash resistivity. The difference between the injection level at low temperatures and that at a high temperature is a measure of excess sulfur trioxide, which will escape from the stack at the higher temperature. If this difference is on the order of 10 ppmV or more, it is likely that a condensation plume will form which may be visible, depending upon the concentration of fly ash in the emitted stream.

It has been found that the simultaneous injection of ammonia (NH_3) with the SO_3 will condition the ash surface to accept resistivity adjustment without excess SO_3 being required [21]. Ammonia FGC tends to overcome this problem by allowing greater adhesion of the residual sulfur trioxide (again, one has to presume that there is a sufficient supply of *natural* SO_3 present) to the acidic ash particle surfaces to optimize its resistivity. This allows for proper fly ash resistivity adjustment without using excess sulfur trioxide. It seems logical that the temperature at which inflection occurs is a function of ash surface conditions - a measure of susceptibility to attachment of acid, perhaps, inasmuch as the lower inflection temperatures occur for ashes having low base-to-acid ratios and the higher points correspond to higher ratios.

III.2.2 IV.2.2 Space-Charge Effect

When ammonia is injected into a gas stream in the presence of the sulfur trioxide a fine fume consisting of a variety of ammonium sulfate particles, all much less than 1 micron in size, is produced. These particles alter the electrical characteristics of the flue gas between the discharge and collecting electrodes and produce a space-charge enhancement of the electric field. This well documented effect arises when fine fume is charged in the precipitator and the electric field is thereby increased. Moderate, strictly controlled quantities of fine particles would therefore, increase the charge level of fly ash particles and the field near the collecting plates. The higher field increases collection efficiency. The space charge effect is usually more pronounced in the front fields than in those following. This happens because a large portion of the particles is collected in the front fields and the remaining small quantity is not sufficient to produce a significant space charge.

III.2.3 Fly Ash Cohesivity Control

Ammonia can generate low melting point substances depending on the H_2SO_4/NH_3 stoichiometric ratio; at low stoichiometric ratios low melting point substances having high moisture absorbency are generated; this promotes cohesion. This cohesion, applied properly and strictly controlled, improves overall precipitator efficiency.

The cohesive properties of fly ash influence stack opacity and precipitator efficiency by agglomerating particles and by reducing re-reentrainment. To simplify, the ammonia combines with sulfur trioxide to form ammonium bisulfate. The melting point for this material, as discussed earlier, is about 147 ^{o}C (297 ^{o}F), so it is semi-liquid at typical flue gas temperatures and acts as a binding agent when mixed with fly ash. Because the agglomerated ash groupings are heavier, rapping losses are minimized.

For high resistivity ashes it has been found that variations of cohesion due to additives are of minor importance to precipitation efficiency. For low resistivity ashes where the use of an additive has little or no effect on resistivity it has been found that changes in efficiency of precipitation are associated with variations of cohesion. High cohesion has resulted in high efficiency due to reduced rapping losses and re-reentrainment or more effective initial capture of particles. The electrical forces of attraction between particles in an ash layer on the collecting electrode in an energized precipitator are the predominant component of the cohesive strength of a highly resistive ash layer and the variation of the mechanical component due to the additive is then relatively unimportant. With low resistivity ash the electrical forces are reduced and may even become repulsive. Under these circumstances mechanical forces causing re-reentrainment become important.

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