Impacts of Ammonia Contamination of Fly Ash on Disposal and Use

Technology Review

Impacts of Ammonia Contamination of Fly Ash on Disposal and Use

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Technical Assessment Report, October 2001

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REPORT SUMMARY

Problems associated with ammoniated ash have become a major concern for coal-fired facilities in recent years as a result of increased use of ammonia-based environmental control technologies. EPRI initiated this research program to assist power producers evaluate and mitigate impacts of ammoniated ash.

Background

American electricity generators are increasingly relying on ammonia-based NOx reduction processes to meet more restrictive air quality emission limits. Flue gas NOx can be converted to elemental nitrogen through either use of urea or ammonia at high temperatures (SNCR, or selective non-catalytic reduction) or ammonia at low temperatures in the presence of a catalyst (SCR, or selective catalytic reduction). These processes can result in a fly ash whose ammonia content is greater than currently acceptable in ash's largest market, the concrete industry. To address this concern, EPRI has initiated this research program.

Objectives

- To collect and determine fly ash's physical and chemical characteristics and adsorption behavior.
- To perform data analysis and correlation of fly ash characteristics to ammonia adsorption behavior and develop prediction calculations for estimating total expected ammonia on ash.
- To determine potential ammonia release problems via air and water associated with ash landfilling, ponding, and other handling procedures.
- To examine beneficiation methods primarily aimed at lowering ammonia on ash, or preventing ammonia deposition to mitigate adverse impacts associated with ammoniated ash.

Approach

Due to the high priority of addressing problems associated with ammoniated ash, as well as the lack of readily available industry data, this technology assessment status report was designed to help end-users evaluate and mitigate impacts of ammoniated ash. Specifically, the project team initiated this program to investigate odor concerns, ash utilization, disposal, and potential groundwater contamination.

Results

This “white paper” first summarizes earlier findings on ammonia deposition rates on fly ash from different coals and the resulting impacts of disposal and utilization. Then it provides an update on the status of current developments in ash beneficiation, with special focus on processes that economically produce a usable ash.

EPRI Perspective

Problems associated with ammoniated ash have become a major concern for coal-fired facilities in recent years as a result of the increased use of ammonia-based environmental control technologies. Therefore, EPRI initiated this research program to assist power producers evaluate and mitigate impacts of ammoniated ash. The project has provided substantial information in each of its four goals (see the Objectives section). This particular assessment paper reports on the status of developing beneficiation options for ammoniated ash.

Keywords

Ammoniated ash
Ash quality
Ash reuse
Ash beneficiation

ABSTRACT

American electricity generators are increasingly relying on ammonia-based NOx reduction processes to meet more restrictive air quality emission limits. Flue gas NOx can be converted to elemental nitrogen through either use of urea or ammonia at high temperatures (SNCR, or selective non-catalytic reduction) or ammonia at low temperatures in the presence of a catalyst (SCR, or selective catalytic reduction). These processes can result in a fly ash whose ammonia content is greater than currently acceptable in ash's largest market, the concrete industry. To address this concern, EPRI has initiated a research program to investigate odor concerns, ash utilization, disposal, and potential groundwater contamination. This "white paper" first summarizes earlier findings on ammonia deposition rates on fly ash from different coals and the resulting impacts of disposal and utilization of this ash. Then it provides an update on the status of current developments in ash beneficiation, with special focus on processes that economically produce a usable ash.

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INTRODUCTION

Most U.S. power producers with coal-fired boilers are being required to reduce emissions of NOx. All new facilities must meet even lower emission limits. Many older units used combustion techniques based on high, single-stage combustion. Under these conditions, NOx emissions are rather high. The use of NOx reduction technologies in electric power plants — combustion system technologies such as low NOx burners (LNB) or overfire air (OFA), or post-combustion system technologies such as selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) — has had a negative impact on the utilization of the resulting coal ash in certain markets. This is largely a result of increased levels of unburned carbon and/or ammonia residuals in the ash.

Combustion modifications seek to reduce the creation of NOx by reducing peak flame temperature and oxygen. These changes also impact important fly ash characteristics. Typically, the unburned carbon (UBC) level in the ash increases. Lower flame temperatures also cause less ash melting. As a consequence, the ash morphology is less spherical. These changes lead to greater variability in fly ash properties that are important to ash users.

Post-combustion controls use chemical reagents (usually ammonia or urea, which deomposes to ammonia in the furnace) to react with NOx and form N_2 and water. Traces of the reagents are adsorbed on the fly ash and can affect by-product markets. A common problem is the odor of ammonia when the ash is wetted.

Problems associated with ammoniated ash have become a major concern for coal-fired facilities in recent years as a result of the increased use of ammonia-based environmental control technologies. Therefore, EPRI initiated a research program to assist power producers evaluate and mitigate the impacts of ammoniated ash. Due to the high priority of this subject, as well as the lack of readily available industry data, this technology assessment status report was conceived to assist end-users in evaluating and mitigating the impacts of ammoniated ash. Four major goals were identified for the overall EPRI effort. The first goal was the collection and determination of fly ash physical and chemical characteristics and adsorption behavior. The second goal was to perform data analysis and correlation of fly ash characteristics to ammonia adsorption behavior and development of prediction calculations for the estimation of total expected ammonia on ash. The third goal was the determination of the potential ammonia release problems via air and water associated with ash landfilling, ponding, and other handling procedures. The fourth goal was the examination of beneficiation methods primarily aimed at lowering the ammonia on ash level, or preventing ammonia deposition to mitigate adverse impacts associated with ammoniated ash. The project has provided substantial information in each of these areas. This particular assessment paper is to report on the status of the development of beneficiation options for the ammoniated ash.

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AMMONIA DEPOSITION ON ASH

In power plants with ammonia-based NOx controls, any ammonia in the flue gas can be deposited on the fly ash as ammonium salts formed by reactions occurring between NH_3 and SO_3 according to the following overall scheme.

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

$2NH_3 + H_2O + SO_3 \rightarrow (NH_4)_2SO_4$ ammonium sulfate

In general, the ammonium salts will form in the temperature window from 145° to 220°C, with ammonium bisulfate being dominant. Ammonium sulfate, mascagnite, is a dry, powdery material. However, ammonium bisulfate is a sticky, partially liquid material that can adhere to surfaces and build up. The rate and amount of deposition will depend on the NH_3 and SO_3 concentrations, velocity and temperatures. Deposition of ammonium salts can cause air heater fouling or even pluggage problems, as well as already mentioned fly ash contamination. While estimates differ, it is usually assumed that as much as 70–80% of the unreacted ammonia is retained in the fly ash.

However, the details of the ammonia adsorption/deposition process involves many complicated chemical and physical reactions. Ammonia adsorption/deposition occurs in a chemical soup in which strong transients are common, such as the variations in flue gas constituent's concentrations, temperatures, and flow regimes. Thus, the ash passes through tremendous variations in physical and chemical regimes in its short residence in the boiler flue gas train to produce the final concentration of ammonia or ammonia salts on the surface of the fly ash. In addition, ammonia deposition/adsorption is likely reversible to a great degree, further complicating the overall process.

The term "adsorption" is used rather loosely to mean ammonia that becomes either attached to the surface of the fly ash as a free ammonia molecule or associated with another entity on the fly ash surface via a pseudo-chemical reaction. This may differ somewhat from common conventions or from the strict definition of adsorption. The term "deposition" is associated with the formation of ammonia salts that react in the gas phase and seek a surface on which to deposit. In some cases, a constituent such as SO_3 may already be present on the fly ash surface prior to reaction with ammonia forming an ammonia salt.

Temperature is a strong driver in both adsorption and deposition. As the flue gas cools, significant amounts of ammonia adsorb onto the fly ash, depleting the flue gas of ammonia and reducing the apparent ammonia slip in the gas phase. Thus, at cool temperatures, where ammonia adsorption/deposition on fly ash has begun to occur, measurement of both the ammonia in the gas phase and the ammonia adsorbed on the ash is necessary to discern the total ammonia slip exiting the upstream process. Significant flue gas cooling, such as occurs across air preheaters, drives ammonia adsorption. In many cases, the ammonia adsorbed on the ash in the cold section of the air preheater or just downstream (partitioned to the ash phase) constitutes a significant portion (50% or greater) of the total amount of ammonia present.

As the flue gas and ash proceed throughout the remaining ductwork and through process equipment such as ESPs or baghouses, additional ammonia partitions to the ash phase or deposits on ductwork as ammonia-sulfur salts. If sufficient quantities of SO_3 are present in the flue gas, then the rate of formation of ammonia salts is high and deposition tends to prevent ammonia emission at the stack. However, to the degree that ammonia slip concentrations exceed SO_3 concentrations and the adsorption capabilities of the fly ash, ammonia may be emitted at the stack (creating concerns over opacity and regulatory limits for ammonia releases).

Under EPRI sponsorship, a comprehensive study was made in 1999 examining the possibility of correlating/predicting the intrinsic ammonia adsorption behavior, as determined in the laboratory, using the various chemical and physical characteristics of the fly ash [2]. Table 2-1 identifies the coals whose ash was tested and Figure 2-1 shows the resulting ammonia adsorption levels on each of these ashes as a function of ammonia concentration (“slip”) in the flue gas.

A number of parameters were found to correlate to the intrinsic ammonia adsorption data, including geometric surface area, major bulk chemical constituents, bulk sulfur content, pH by the 95% ethanol method, and unburned carbon. Linear correlations were determined for each gas-phase ammonia level in the bench-scale adsorption experiments. The five best parameters were chosen for each correlation. A typical correlation/predictor equation looks like this:

$$NH_3 = -7.2 - (0.684 \bullet Al) - (11.056 \bullet P) - (5.342 \bullet K) + (1.790 \bullet Si) + (3.131 \bullet S)$$

The above equation was for 1 ppmv NH_3 slip and showed a correlation coefficient of 0.94. The element concentrations are expressed in ppm.

Interestingly, appreciable amounts of ammonia may be released to the combustion air as the flue gas passes through the air preheater. Thus, a material balance around an air heater must include ammonia released to the air-side. It is believed that this ammonia, which is returned to the boiler, is ultimately thermally destroyed in the combustion process.

The measurement of ammonia on ash is not without complications. In liquid form, ammonia measurement can be done using several techniques, including titration, colorimetric, enzymatic and electrochemical methods. The real issue however is determining the level of ammonia released from the ash to the air. There are two methodologies for doing this: (1) using a solid sorbent within a sealed glass tube; and (2) using a trap system where the ammonia is captured in an aqueous acid solution. Based on discussions with the ash marketing firms, the ammonia detection tubes, which contain a solid sorbent with an indicator that changes color, have been found to be useful for “spot samples” of the work areas. The limitations on the method are that the sampling volume is very small (about 100 cm^3) so the air sampling syringe has to pull the air being sampled through at a specific rate to be accurate. ISG Resources reported that they have observed that different brands of tubes produce significantly different readings, but that the repeatability is good for each brand.

Table 2-1
Ash Sample Sources for EPRI Ammonia Project

Sample Name	Coal Type	Coal Rank	Source	SO_3 Injection	Firing Config.
Baldwin	Illinois #6	Bituminous, High Vol. C	Illinois Power, Baldwin Station	No	Cyclone
Bowen	Eastern compliance coal, Cyprus Amax Coal Co., Sigmon Mine	Bituminous, High Vol. B	Georgia Power, Plant Bowen, Unit #3	Yes (7 ppmv)	Tangential
Cardinal I	Pittsburgh #8	Bituminous, High Vol. B	AEP, Cardinal Plant, Unit #1	No	Cell/Wall Hybrid
Cardinal II	Pittsburgh #8	Bituminous, High Vol. B	AEP, Cardinal Plant, Unit #1	No	Cell/Wall Hybrid w/Low NOx burners
El Cerrejon	South American (Venezuela)	Bituminous, High Vol. B	PowerGen Test Combustor	No	Tangential/ Test Combustor
Lone Mountain	Appalachia Compliance coal, Virginia, Arch Coal, Inc.	Bituminous, High Vol. A	Southern Research Test Combustor	No	Tangential/ Test Combustor
Miller	Powder River Basin, Belle Ayr Mine	Subbitum.C	Alabama Power, Plant Miller, Unit #3	No	Wall
Paradise	Powder River Basin	Subbitum. B	TVA Paradise Plant	No	Cyclone
Pleasant Prairie	Powder River Basin, Caballo Mine	Subbitum. C	Wisc. Electric, Pleasant Prairie Power Plant, Units #1 and #2	Yes (6 ppmv)	Wall
Sioux I	Blend: 83% PRB, 17% Illinois Bituminous	Blend	Ameren Sioux Plant, Unit #1	Yes (8-10 ppmv)	Conventional Cyclone
Sioux II	Blend: 83% PRB, 17% Illinois Bituminous	Blend	Ameren Sioux Plant, Unit #2	No	Conventional Cyclone w/OFA
Stanton	Eastern Kentucky, Blend, Low Sulfur Eastern	Bituminous, High Vol. A	Orlando Utilities Stanton Power Station, Unit #2	No	Wall
Yates	Eastern Low Sulfur Blend, Wise County, Virginia	Bituminous, High Vol. A	Georgia Power, Plant Yates, Unit #1	No	T-Fired

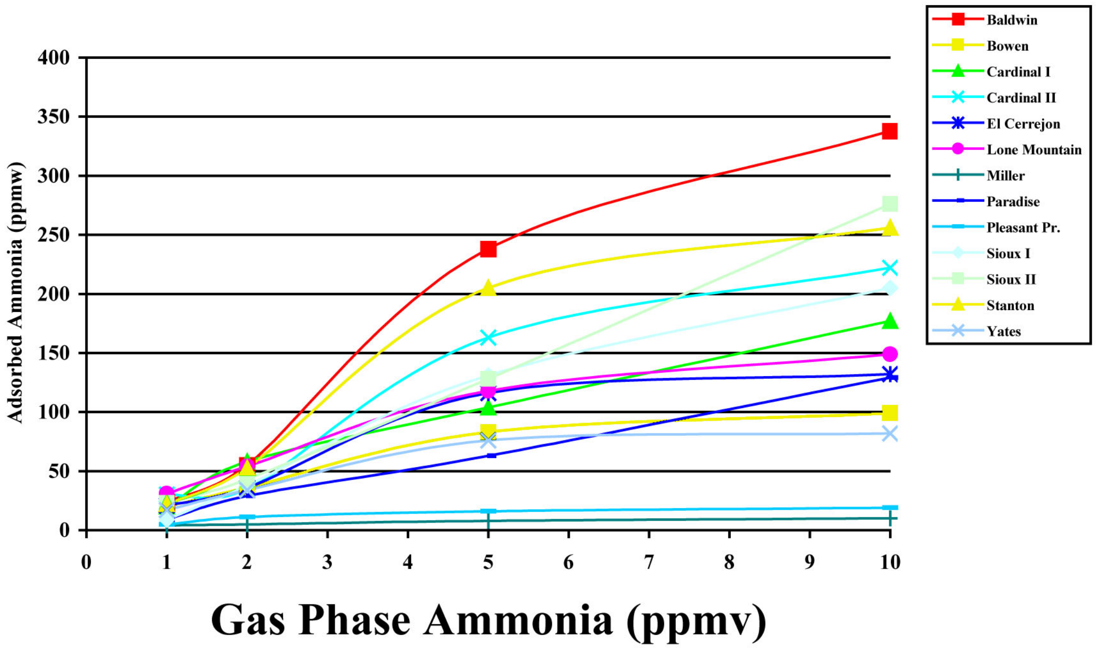

Figure 2-1
Adsorbed Ammonia vs. Gas Phase Ammonia Level

The occupational safety regulatory agencies, namely OSHA and NIOSH, recommend the use of CISA (carbon impregnated with sulfuric acid) tubes for the sampling of ammonia in the workplace. It is more accurate than the small tubes mentioned above, since a much larger volume of air can be sampled (24 liters vs 100 cm^3). The ammonia in the air is sorbed onto the CISA tubes as ammonium sulfate. These regulatory approved methods, too, have their shortcomings, given the levels of ammonia that can be present in the ashes. The CISA tubes do not have a concentration indicator, and require frequent replacement of the adsorptive capacity.

3

AMMONIA IMPACTS ON ASH UTILIZATION

The sale of fly ash is an important component of ash management at many utilities. It represents both revenue enhancement and reduced disposal costs. Some utilities are currently reporting lost ash sales due to off-specification ash (high LOI) or detectable ammonia contamination. Consequently, consideration needs to be given to the prevention or mitigation of the impact of ash contamination on important and sensitive utilization markets, particularly cement and concrete applications.

Earlier Investigations – A Summary

A 1996 EPRI study investigated the impacts of the post-combustion NOx technologies on ash use [1]. Key findings of this study relative to the ammonia issue were as follows:

- Ash with high ammonia levels may not be acceptable as a cement feedstock. Although the ammonia does not impact the strength of the resulting concrete, its presence generates an odor, and hence, nuisance conditions for workers during placement. Construction and other bulk applications are not impacted unless personnel exposure in enclosed spaces is possible.
- With suitable mitigation measures, low-NOx ashes can still be used in existing pozzolan and concrete markets—albeit at a cost.
- Disposal costs for low-NOx ash can increase due to lower bulk density. The lower density requires more water for compaction and greater volumes; landfills will not last as long.
- Methods are known for beneficiating high NH_3 contaminated fly ash.

Six fly ash properties that are important for determining ash usability can be affected by the current generation of combustion and post-combustion NOx reduction technologies.

1. Carbon content
2. Particle properties
3. Mineralogical properties
4. Reactivity
5. Variability
6. Contamination with ammonia

This paper will focus only on the ammonia issue. Experience to date in North America with ammonia-contaminated ash has come largely from plants using it as a precipitator aid. In many cases, ash from these sites was unmarketable. Although post combustion NOx processes will likely lead to lower levels of ammonia contamination, it is likely that ash marketers will be very wary of a given source until it is demonstrated that the level of contamination is both stable and below a certain critical level (to be determined). Whether ammonia contamination also leads to problems with ash disposal is being addressed by EPRI's Environment Sector, especially for ponded ash.

Market Acceptance of Ammoniated Ash

The acceptance of ammoniated ash by the ready–mix concrete industry is a function of both technical and economic factors, as well as institutional barriers. First the relative supply of ash that does not have an ammonia odor will influence its acceptance. If clean ash is available at the same price and quantities, then the ammoniated ash will not be accepted. During the peak construction season there are often shortages of ash in local markets, due to inadequate silo storage capacity and limitations on the number of trucks in service hauling ash from power plants to the ready-mix plants. A similar condition existed four or five years ago when many power plants first installed deNOx equipment which resulted in ashes with much higher LOI levels than had been the usual levels from the plants. In that case, although the ASTM standard (C618) allows ashes up to 6% LOI for use in concrete, the "marketplace" had not allowed it to go above 4%, due to concerns over air entrainment variability as a result of the sensitivity of the AEA admixtures to carbon. Regional differences in acceptance can be even greater. For example in parts of Colorado, where Class C (Powder River Basin) coal fly ashes are common, the ready-mix contractors get upset when the LOI doubles from 0.5% to 1.0%. Yet this same ash would be considered of exceptional quality in parts of the US where Class F ashes commonly in the 3 to 4% range is what is generally available.

The next variable to consider is the availability of other substitute materials that could be brought in to replace its use in concrete. Ground granulated blast furnace slag (GGBFS) is available in some parts of the eastern US and has been found to be as useful as coal fly ash in concrete applications. So its (GGBFS) availability, distance to local sources, and price will impact the acceptance of the ammoniated ash.

The ash marketers were surveyed in August 2001 to obtain an update on the acceptance of the ashes from NOx control systems. In general the "market acceptance" level of marginal ashes from the standpoint of LOI has increased from what was previously an upper limit of 4% to higher levels in some areas. The ammonia issue is not an entirely new one with the advent of the SCR and SNCR systems. Many units have used ammonia for opacity control in ESPs for several years. Southeastern Fly Ash is one such ash marketer that has experienced this ammonia problem from the ESPs. The solution has been to use a QA program using the quick ammonia analysis GasTec^{TM} capsules, and reject the ash when the ammonia levels exceed 20 ppm [19]. Many of these marginal ashes are now finding their way into the flowable fill market. In this application, when you are using upwards of 600 lbs of ash per yard, the ammonia off-gassing could be significant if ammonia concentrations are not kept below 20 ppm. Another ash marketer (Boral Materials) in the Texas region reported that they have not experienced any significant problems with ammonia laden ashes. Russell Hill reported that ammonia levels up to 60 ppm appear to be accepted [22].

The ash marketers surveyed did not report any changes to the existing ash handling systems after the addition of SCR systems. The sites have generally opted to maintain unit operations in their current configuration.

In summary, evidence to date suggests that the acceptable level of ammonia in ash that the marketplace will accept is in the range of 20 to 60 ppm. This compares to the level of 50 to 100 ppm that is standard practice in Europe. Although ash buyers have expressed "philosophical concerns" about the presence of ammonia on ash, there does not appear to be a significant impact on ash quality or beneficial use potential.

Quality control of the ash appears to be a key concern. The use of the GasTec™ capsules for the measurement of the ammonia levels gives the ash marketers a quick and easy method for measurement of the ammonia levels.

Air Concentrations of Ammonia Associated with Ammoniated Fly Ash Use

Some quick calculations can be performed to estimate the total amount of ammonia that is available from fly ash and the resulting possible air ammonia concentration that can result from the evolution of that ammonia. For example, if the assumption is made that fly ash contains 100 ppm by weight of ammonia, then one ton of fly ash, evolving all of the ammonia present, can produce 90,000 cubic feet of air (at 68 °F, 1 atm) that contains 50 ppmv of ammonia (the upper odor threshold). This demonstrates that most enclosed ash storage or transport facilities have the potential to produce quite high concentrations of ammonia in air if conditions are conducive to the evolution of ammonia from the ash [1].

A more likely scenario for generating high concentrations of ammonia is in the pouring of concrete. For instance, if we use the above warehouse (15 m by 15 m by 5 m high) and pour concrete 0.3 m thick with a nominal fly ash concentration of 100 ppmv, the calculation shows that an air concentration of 2,000 mg/L ammonia is possible, assuming that all of the ammonia on the ash (100 mg/L) is evolved into the warehouse air space.

An ongoing project funded by the Department of Energy (DE-FC26-00NT40908) and conducted by the University of Kentucky Center for Applied Energy Research is investigating the effects of ammonia injection on the resulting concrete mixes. In that study an experimental set-up was designed to measure ammonia loss from the cement mortar over time, using a trap solution which could be periodically measured during curing of the cement mortar. The effects of various water to cementitious ratios on the ammonia loss rate are being examined. The tentative results indicate that, unlike aqueous solutions, the rate of ammonia loss occurs in two phases: a rapid rate followed by a much slower linear rate that began after about 24 hours of curing and persisted throughout the 3 week test period. The surprise result was that a good portion (greater than 80%) of the ammonia was calculated to have remained in the mortar. This has implications for some applications like basements were periodic wetting during rainfall events, could create new ammonia "events" to upset the end-users.

These two calculations demonstrate that at least from a theoretical standpoint, the quantities of ammonia commonly present in ash associated with ammonia-based deNOx processes do have the potential to cause nuisance problems.

Ammonia Release Test Methods

In a Department of Energy study reported in a paper presented by Gary Brendel at the 2001 ACAA Symposium, the ammonia release from fly ash in a closed system was evaluated using Pyrex columns that were 60 cm long and 4.25 cm in diameter. The column of fly ash and water was supported by a porous glass frit overlain by 50 g of washed, graded sand. Fly ash (135 g) was slurried with 300 ml of distilled water in a polyethylene bottle and the mixture poured into the Pyrex column, followed by washing the remaining fly ash from the bottle and column sides with 100 ml of distilled water. This procedure yielded a total ash content of 25 % by weight. A two-hole rubber stopper was fitted tightly over the opening at the top of the column, and the holes sealed using small stoppers. Eight to ten columns were prepared for each ash such that periodic measurements could be made over the course of two (2) months. At each specified interval, ammonia in the sealed head-space was measured using GasTec™ ammonia-sensing tubes, followed by draining the water from the bottom of the column into an Erlenmeyer flask. Un-ionized NH3 was measured in solution using the Orion ammonia electrode described above, while NH4+ ion was estimated using an Orion 93-18 ammonium-specific electrode [11].

4

STORAGE AND DISPOSAL OF AMMONIA-CONTAMINATED FLY ASH

Complications Resulting from Storage/Disposal of Ammoniated Ash

Low levels of ammonia exposure are common due to its pervasiveness in nature. Ammonia is frequently found in water, soil, and air and is important biologically as a source of nitrogen for plants and animals. The majority of environmental ammonia occurs as a result of the natural breakdown of manure and decaying plants and animals. Man-made releases of ammonia constitute a very small proportion of the overall ammonia found in the environment. Approximately 80% of all man-made ammonia is used as fertilizer, with a third of that applied directly as pure ammonia, and the remainder used in ammonium containing fertilizers. Normal ambient concentrations of ammonia are as follows; soil 1-5 ppm, air 1-5 ppb, and rivers and bays 6 ppm. Ambient environmental ammonia levels are generally the highest during the summer and spring [2, 3].

Ammonia has a relatively short environmental life. In soil and water, plants and microorganisms readily take up ammonia. Soil fertilization produces initially high levels of soil ammonia but these levels decrease to very low concentrations in a few days. In the air, ammonia will remain for about one week before it is removed by natural processes [2, 3].

It has long been known that the wetting of ammonia-contaminated ash will cause the ammonia to volatilize. The experimental data show that even small amounts of water, such as that contained in very humid air, promote ammonia volatilization. This, however, brings up some important points concerning ammonia volatilization. The amount of ammonia vaporized and the degree of ammonia lost from a volume of ash is highly dependent on mass transfer, both from the standpoint of moisture reaching the ash particles and ammonia evolving and reaching surrounding air. For instance, in a large mass of ash, although moisture contact from ambient air at the bulk surface of the ash may cause volatilization to occur readily, it is unlikely that moisture can easily reach the depths of the ash mass, effectively preventing much of the potential for ammonia volatilization. In addition, it is likely that ashes of different compositions behave differently in terms of the amount of moisture necessary for volatilization to occur.

One goal of the EPRI study on ammonia deposition on fly ash was to estimate the release of ammonia to the environment when ammonia-contaminated ash is disposed in landfills or ponds [2]. This goal was met primarily by performing engineering calculations to examine potential air and water ammonia concentrations, and leaching tests to determine the effect of ammonia on the leachability of fly ash constituents. The calculations of theoretical maximum air releases at landfills showed that the potential exists for unacceptably high ammonia in air concentrations if the physical conditions are conducive. This is most likely to occur during a heavy rain with minimal winds [14]. In addition, both ash landfill runoff and leachate have the potential for very high ammonia concentrations. Situations where pond ammonia hold-up occurs may result in highly elevated ammonia concentrations within the pond and at the pond outfall.

Fate of Ammonia in Groundwater

The fate of NH_3 in groundwater needs to be investigated further. As the schematic drawing in Figure 4-1 indicates, ammonia can reach groundwaters via several pathways.

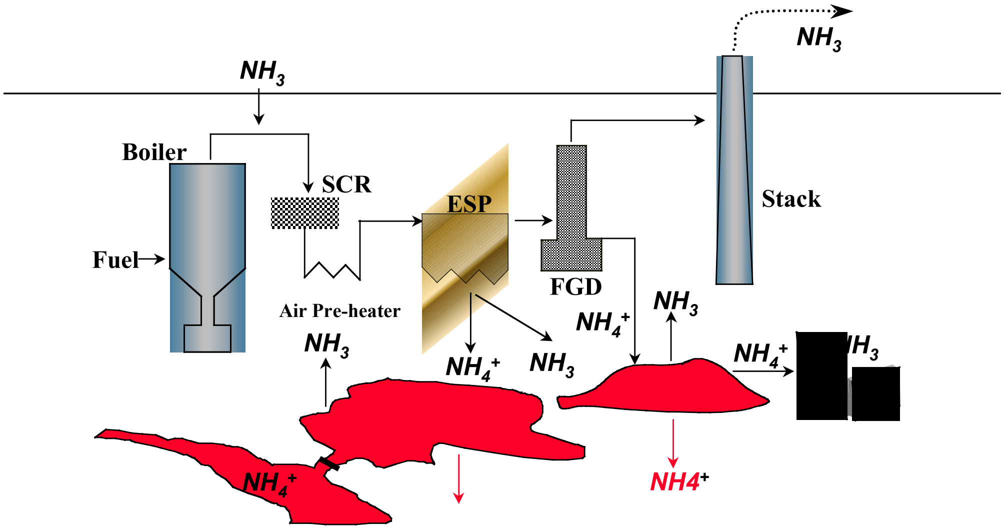

Figure 4-1
Pathways of Ammonia in a Power Plant Environment

The potential concerns are what impact the release will have on drinking water quality, which has a 10 mg/L NO_3 and a 1 mg/L NO_2 limit. Any seepage to surface water could have an impact on nutrient loading, with the resulting potential for eutrophication of the water body.

Preliminary calculations showed that there is a potential for outfall ammonia concentrations from ponds to exceed common industrial regulatory limits. In addition, physical situations where pond hold-up occurs may result in highly elevated ammonia concentrations, at least for a period of a few days. Ash landfill runoff and leachate both have the potential for very high ammonia concentrations since the relative fly ash to water ratio is high.

A number of factors affect nitrogen mobility in soils, including:

- Initial concentrations and forms
- pH
- Oxygen
- Microbial activity
- Soil type
- Moisture conditions

The analyses performed in the EPRI work to date concerning potential landfill and pond releases has been rather preliminary, in keeping with the initial stages of this research. However, the calculations have shown that the potential does exist for ammonia releases in both air and water, which could be quite problematic. This indicates the need for more detailed analyses and simulation calculations which can more adequately predict the potential ammonia concentrations in air and water, and the resulting environmental impacts. Experiments now underway in an EPRI research project at the University of Alabama at Birmingham are examining the potential rates of ammonia evolution from ashes under conditions mimicking natural landfilling. Additional calculation methods will be devised to assess impacts from ammonia releases for landfills, ponds, and special handling procedures such as ash sluicing, conditioning, and the use of ash in industrial applications. The potential for ammonia release to the atmosphere from ponds, landfills and ash impoundments appears to be driven almost exclusively from the pH of the aqueous solution. When the pH of the pond is below 7 to 8, no odors or significant releases are observed, and when their pH is above 9 to 10 all of the ammonia present is released creating nuisance odor conditions.

5

CURRENT PROCESSES FOR AMMONIA REMOVAL

Concern over the removal of ammonia (free ammonia or ammonia compounds, subsequently termed “ammonia”) from fly ash is a relatively new phenomenon for the power industry. This is a result of the relatively recent implementation of ammonia-based NOx removal processes and the ammonia deposition on fly ash that occurs from these processes.

A number of processes were discovered in the literature during the EPRI study for removing ammonia from fly ash or for “fixing” the ammonia on fly ash or similar substances to prevent its evolution [2]. Although many wet processes were discovered, these processes were generally thought to be inapplicable due to the expected destruction of the pozzolanic activity associated with wet ash processing (this assessment will be reviewed in 2002). The dry processes discovered all rely on the thermal removal of ammonia and thus require significant mechanical and thermal processing. This likely makes the currently described dry processes unattractive due to cost. Fixation technologies are available, but most have never been demonstrated on fly ash. Further research is required to develop a process which meets all technical and economic criteria for a viable ammonia removal or fixing process.

Ammonia Removal

Because of the value associated with dry fly ash, wet ammonia removal processes are viewed as technologies of last resort. The wet technologies are more likely to be used to minimize adverse ammonia releases prior to the disposal of fly ash. All dry ammonia removal technologies that have been developed to date rely on some combination of the following: heat, addition of small amounts of water, and addition of alkaline materials. Due to their energy intensive nature and high mechanical processing and handling requirements, these processes are viewed as high cost and rather unsophisticated. The following is the criteria for assessment of ammonia removal processes employed in the 1999 EPRI investigation [2].

1. The process must occur under conditions in which the resulting pozzolanic activity of the fly ash is not compromised.
2. Mechanical processing of the ash must be minimized to avoid undue additional equipment and labor and the resulting costs associated with procuring, maintaining, and operating the equipment.
3. The process must be simple and effective and thus not require a great deal of testing or oversight to ensure adequate, consistent ammonia removal.
4. The process must be very low in overall cost to ensure continued economic benefits from ash sales.

Several processes are available which strip absorbed gaseous ammonia from aqueous solutions. Both patented and established common practice processes are described in the literature. None of the stripping processes that work from aqueous solutions are relevant to the removal of ammonia from dry fly ash. The following ammonia removal processes were identified in this project.

1. ReUse Technology ASH PRO^{TM} Ammonia Removal Process [9].
2. Harald and Ruegg Thermal Process [10].
3. High Temperature Dry Ammonia Removal Process [11].
4. Semi-Dry Ammonia Removal Processes [12, 13].
5. Reburning in a dedicated FBC Unit
6. Washing/Humidification
7. Ozone Treatment
8. Ambient Wet Aggregate Production
9. Reburning in an Ash Fuel System
10. Lightweight Aggregate Process
11. Ammonia Liberation Process

A process has been identified during the just completed EPRI project, which is designed to scavenge ammonia in the flue gas, and destroy it prior to its adsorption or deposition on the fly ash particles [2]. Such a process would have very desirable characteristics: low cost, operational simplicity, low capital equipment and maintenance requirements, and ancillary benefits associated with preventing ammonium bisulfate deposition and the resulting air preheater fouling. A patent has been applied for this process. Some preliminary experiments were performed using a test combustor while burning natural gas to assess the potential of this process for removing ammonia. These tests were consequently performed in the absence on fly ash. The results showed that the gas-phase reaction of the scavenger material and ammonia was too slow to accomplish appreciable ammonia destruction. However, future tests are planned with fly ash present to more closely simulate actual conditions. It is hoped that the presence of fly ash in the flue gas stream will enhance the ability of the scavenger material to react with the fly ash via catalyzed reactions.

Commercialization Status of Ammonia Removal Methods

The interest in the ammonia issue and its potential impact on the ash reuse market was apparent at the January 2001 14th International ACAA CCP Use Symposium, in San Antonio [11-18]. Two entire half-day sessions were devoted to papers on the research in this area. Most methods discussed were thermal destruction methods such as the carbon burnout (CBO); microwave; or combinations of moisture and a chemical admixture using alkali (STI process); and conventional thermal destruction. Some general observations from these papers are: (1) the thermal destruction processes appear to suffer a cost disadvantage due to the price of natural gas. The typical amount mentioned was $3 to $4/ton ash for energy costs; (2) Combination processes like the CBO have potential advantage to remove both NH_3 and carbon; (3) Passivation methods using a strong oxidizer like ozone are still in the research stage, but hold promise due to their inherent low energy cost; and (4) the process that adds an alkali salt to the concrete when it is in the mixer raises questions about the risk of flash set of the concrete or corrosion problems with rebar.

Southeastern Fly Ash appears to be relying more on the Carbon Burnout technology [24] for beneficiation of both carbon and ammonia, as well as blending of high quality ashes with those containing higher LOI or ammonia levels to keep the resulting product within specifications.

ISG Resources, Inc., the nations largest ash marketing firm, reported that the ammoniated ash issue has not had a significant impact on its sale of ash to the concrete market [20]. The full impact of the NOx control systems has yet to be felt in the ash market, since many of the large base-loaded plants have not yet completed their retrofit of SCR or SNCR post-combustion NOx control systems.

Separation Technologies, Inc (STI) has developed a chemical to alleviate the ammonia odor problem. This calcium based alkali chemical compound ($Ca(OH)_2$) was detailed by Gasiorowski's paper presented at the aforementioned ACAA 2001 Symposium [16]. The process is performed at ambient temperature. The recovered fly ash met all chemical and physical requirements of ASTM C 618. Pilot plant trials conducted by STI have demonstrated the process to reduce the ammonia concentration on contaminated ash containing up to 1000 mg NH_3 / kg to less than 20 mg / kg at a rate of 3000 lb / hour (1,363 Kg/h). Design of a commercial size operation is underway which will handle 40 tons per hour of contaminated ash. The chemical admixture was able to reduce the ammonia content from 250 mg/kg to 20 mg/kg by the continuous process. STI has also developed a different delivery system where this chemical admixture can be added directly into the ready-mix trucks to alleviate the ammonia odor problem.

The ReUse Technology ASH PRO^{TM} ammonia removal process [9]. mentioned earlier has seen no moves toward commercialization over the past year. The company spokesmen (Robert Waldrup) indicated that the process had been abandoned. Their focus has been on the co-generation utility market which has smaller units that are used for peaking power production. As a result of this, the high variability of the LOI in the ashes make their use problematical. For this reason ReUse Technology has gone after agricultural applications for the high LOI and ammoniated ashes. The ammonia does not create problems in these applications; in fact the added nitrogen in the applications on crops such as peanuts are beneficial. The company also reported using a combination of the NOx ashes with scrubber sludge for peanut crops [21].

The thermal process development seems to be led by Wisconsin Electric Power Company (WEPCo), who has recently developed two processes that were described by Bruce Ramme at the Mega Symposium in Arlington Heights (Chicago), IL, August 20-23, 2001 [23]. They have been demonstrated at various power plants operated by WEPCo. The first is called the "ash fuel reburn process" and has been issued a U.S. Patent (No. 5,992,336). A small proportion (1 to 3.5%) of high LOI and ammoniated ashes is added in a fine particle condition to the burners of a pulverized coal boiler firing a reactive coal (i.e., one that produces a very low LOI ash). The resulting coal ash has an overall LOI level of 1 to 2% or less, and the ammonia appears to be oxidized in the furnace. Depending on how the combustion process is managed in the burner(s) receiving the recycled ash, this ammonia may or may not increase furnace NOx emissions. The advantage of the process is that the fuel value that existed in the high LOI ash is used for steam generation.

The second process is a truer ammonia removal process. Developed to date as a small-scale prototype, it also reduces carbon in the ash. WEPCo's research indicated that no less than seven ammonia species are present in the contaminants from NOx reduction systems, each with a different disassociation temperature profile. The controlling temperature is the highest required by any of the compounds – 813°F (434°C) for the bisulfate and sulfate forms. The process preheats the ash and feeds it to a processing bed where the temperature is increased to 1,000°F (538°C) with hot fluidizing air. The fluidizing air is supplied by a natural gas fired burner and forced through a porous metal media. The ash leaves the processing bed and is cooled in a heat exchanger, while the contaminated air is first passed through a baghouse to capture any fugitive ash and then passed back into either the furnace or the boiler's SCR. Pilot test results on a number of different ashes with varying carbon and ammonia levels have shown it is able to reduce ammonia levels from 160 mg/kg to less than 2 mg/kg (ppmw). According to WEPCo, the costs for a small (50 ton/hr) system would be about $3.60/ton ash processed.

Natural gas prices can have a significant impact on the economic viability of these processes. For example, the light aggregate production facility operated by Minergy, Inc for WEPCo has ceased production do to high natural gas prices to fuel the kiln.

The carbon burnout process (CBO) seems to be gaining market acceptance for both LOI reduction and for ammonia removal. A recent presentation [24] on this technology was given by James Keppeler of Progress Materials, Inc. at the January 2001 ACAA Symposium focuses on its carbon removal performance of the first full-scale application at the Wateree Station of South Carolina Electric and Gas. The author also reported that Progress Materials conducted a CBO pilot plant test program on over 25 tons of high-carbon fly ash containing several hundred parts per million of ammonia. This work demonstrated that, even without process flow changes, product ash from the Carbon Burn-Out fluid bed is both low-carbon and ammonia-free. Long residence times (particles average about 45 minutes in the fluid bed) together with average temperatures in the 1350° F range promote those reductions. At these combustion temperatures the ammonia is decomposed. Santee Cooper's Winyah Station will be the site of the next CBO, slated to be in service in 2002. Among the design enhancements to be incorporated are improved feed ash blending facilities, elimination of above-bed burners (which were found to be unnecessary) and an integrated fluid bed rather than two separate cells. Also, this second generation CBO plant has been designed with an improved air distribution plate seal system, and eliminated "double dump" valves used to control ash flow to the exhaust duct for transport to the cyclone collector / baghouse. All of these improvements favor an even more economical means of using this technology for both LOI and ammonia reduction.

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CONCLUSIONS

Earlier EPRI investigations have shown that:

- In laboratory tests, ammonia adsorption by fly ash depends on the ash chemistry (i.e., coal source)
- Under field conditions, ammonia adsorption is also be affected by the SO_3 concentration and temperature history of the flue gas
- There is a potential for unacceptably high ammonia concentrations in air, pond water, pond discharge water, and landfill runoff and leachate. (Planned tests will examine in more detail the ammonia evolution behavior of fly ash under conditions similar to either water sluicing to a pond or landfilling and exposure to weathering.)
- Ammonia leaches readily from fly ash and appears to have fairly high soil mobility; biological activity is also high

Some utilities are currently reporting lost ash sales due to detectable ammonia contamination (also due to high unburned carbon levels). The ash market seems to limit ammonia-in-ash concentrations to 20 to 50 ppmw; this compares to levels of 50 to 100 ppmw in Germany. Ammonia does not impact the performance of concrete, although nuisance odors during placement of the concrete could cause potential users to seek other supplementary cementing materials like glass furnace slags in the competitive marketplace.

A number of processes for removing ammonia from fly ash are currently under development or just now being offered commercially, and several appear technically feasible. The challenge is to find processes that do not alter the pozzolonic properties of the resulting ash, are not too energy intensive, and do not add a chemical that can deteriorate some performance characteristics of concrete made using the ash – i.e., that meet both usability and economic constraints. Planned tests will evaluate several processes for their technical feasibility, including processes being developed by others.

7

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