Dendy, Lewis H.

From: Nelson, Debra GRE/MG [dnelson@grenergy.com]
Sent: Friday, August 08, 2008 3:19 PM
To: Dendy, Lewis H.
Cc: Roth, Mary Jo GRE/MG; Stockdill, Diane GRE/CCS
Subject: RE: Coal Creek BART proposal
Attachments: BART NH4 in Ash.doc

Lew,
Here is our response to Mr. Shepherds inquiries about ammonia in fly ash.

Thank you.

Deb Nelson
Environmental Services
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Response to question about ammonia in fly ash

Currently Coal Creek Station fly ash is highly desirable due to the physical and chemical characteristics which enable it to create high quality concrete. The ASTM standard states the purchaser shall specify any supplementary optional physical requirements. Due to the odoriferous nature of ammoniated ash it is a characteristic likely to be limited in purchase orders. Ash with high levels of ammonia is less desirable by concrete manufacturers due to the strong odor released from the ammoniated ash. Ammonia release from ash impacts ambient air quality and indoor air quality or presents a direct exposure hazard. Fly ash will emit ammonia as the ash is transferred, transported or mixed and concrete will emit ammonia – as the ammonia "off-gases" or volatilizes when the fly ash is transferred, transported, or mixed for concrete. Tests conducted under DOE funding suggest that the ammonia loss in concrete occurs in two phases: first a rapid initial release within 24 hrs.; then a slower linear release rate – which occurred throughout the 3 week test period. Based on the measurements and calculations it was determined that over 80% of the ammonia remained in the concrete at the conclusion of the test period. This leaves a potential for ammonia release during future rainfall events when the water volatilizes the ammonia. This could be very hazardous in occupied spaces. [See the exposure description below.] The study does not encourage the use of ammoniated ash, but recommends that ammonia concentration in fly ash be kept below 100 mg/kg for concrete used in enclosed spaces and below 200 mg/kg for concrete used in other applications.

Ammonia is considered a toxic air pollutant by the environmental and health regulatory agencies in North Dakota, Minnesota, and other surrounding states for which the ammoniated ash would be handled and processed. In North Dakota, the Department of Health's Air Toxics Policy establishes acute health risk standards. The ambient ammonia concentration thresholds are 0.49 mg/m^3 (0.66 ppm) on a 1-hour average and 0.35 mg/m^3 (0.47 ppm) on an 8-hour average. Any concentration above these levels would exceed the State's acceptable level of non-carcinogenic risk.

Ammonia is considered an upper respiratory irritant for inhalation health effects. The EPA's Integrated Risk Information System (IRIS) has a reference concentration (RfC) of 0.1 mg/m^3 (0.14 ppm) for acute exposure to ammonia, and the Occupational Safety and Health Administration (OSHA) has set an 8-hour exposure limit of 25 ppm and a 15-minute exposure limit of 35 ppm.

A majority of the Coal Creek Station market resides in the upper Midwest. Fly ash created during the off season for construction is either used in internal enclosed applications or is stored (e.g. pre-cast concrete blocks or panels). The storage and transfer of ammoniated ash in enclosed facilities could have the potential to produce high concentrations of ammonia in the occupied buildings. In an example from an Electric Power Research Institute paper, 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). When given the option concrete manufacturers will purchase a non ammoniated ash over the ammoniated ash due to the odor produced when mixing and pouring the concrete.

In addition to the stated health risk criteria, ammonia is a highly odoriferous compound that is regulated by many localities and states, including in North Dakota (see NDCC 23-25-11). Of particular concern is the risk of odors that disperse to nearby locations off-site from Coal Creek Station. Blue Flint Ethanol is located next to Coal Creek Station, and their property is located 850 feet from the fly ash dome and related ash handling activities. Volatilized ammonia represents an odor and health concern at areas proximate to the plant and at endpoint locations where the ash/cement is used. These risks would need to be better understood and addressed before the ash, as modified, is beneficially used for high quality concrete rather than go to a landfill or other disposition.

Dendy, Lewis H.

From: Nelson, Debra GRE/MG [dnelson@grenergy.com]
Sent: Wednesday, September 17, 2008 2:22 PM
To: Dendy, Lewis H.
Cc: Roth, Mary Jo GRE/MG; Stockdill, Diane GRE/CCS
Subject: Additional Information on Ammonia in Fly Ash

Lew,

Great River Energy respectfully submits the following text in response to your request for additional information on the concentration of ammonia in fly ash during the August 21, 2008 conference call. A review of the papers and studies completed on ammoniated ash from two of the top electric power research organizations in the US (EPRI and UND-EERC) found that very little if any work has been completed to date with respect to lignite coal combustion and SCR or SNCR NO_X control equipment. GRE made direct requests of individuals in charge of research in this area. Several studies have been conducted but at least one was inconclusive for lignite fly ash. The SCR catalyst research included in the original Coal Creek Station BART analysis in Appendix G had conclusive information about SCR use with lignite coal combustion but only evaluated the performance of the SCR catalyst and mercury ionization. It did not include an analysis of the ammonia in the ash. One other study by EERC was evaluating the leaching of specific constituents in ammoniated fly ash but the results were not conclusive for ND lignite since the method used to ammoniate the fly ash was unsuccessful. Additional studies were not discovered. Predicting the ammonia in ash is extremely difficult due to the many factors influencing the adsorption and deposition of ammonia in fly ash. Some of the factors include coal processing – fineness, coal heating value, ash mineral composition, ammonia slip, and other boiler settings responsible for influencing the formation of SO_3 in the flue gas. For example, SO_3 production promotes the formation of ammonium sulfates driving the ammonia toward fly ash deposition; therefore any plant operating conditions which influence SO_3 production would also influence the adsorption and deposition of ammonia in fly ash. Each of these physical and combustion characteristics is very different between the various ranks of coals. One study illustrated the variability of ammonia adsorption throughout an ESP with concentrations ranging from 51 ppm_w to 740 ppm_w. (This test used a 4 ppm_w injection rate for ammonia and also has SO_3 injection.) The same study also found the ammonia concentration variability within an ESP to range from 3 ppm_w to 30 ppm_w from another SCR controlled unit. Both tests were conducted at facilities burning eastern bituminous coal. This specific example illustrates the site specific qualities associated with ammonia injection pollution control technology.

If you require further information please feel free to give me a call. Thank you.

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PROJECT FACTS

UNIVERSITY OF KENTUCKY
CENTER FOR APPLIED ENERGY RESEARCH

AMMONIATED FLY ASH

PARTICIPANTS

University of Kentucky
Center for Applied Energy Research
Boral Material Techn.
ISG Resources
LaFarge North America
Southern Company Serv.

SPONSORS

US Department of Energy

PROJECT VALUE

DOE Cost: $149,815
Prime Contractor Cost Share: $90,511
Partner Cost Share: $60,000

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Objective

The goal of this project was to develop practical guidelines for handling and using ammoniated fly ash in concrete, in order to prevent a decrease in the use of fly ash for this application. The objective was to determine the amount of ammonia that is released, over the short- and long-term, from concrete that contains ammoniated fly ash.

Background

The Clean Air Act Amendments of 1990 require large reductions in NO_x emissions from coal-fired electric utility boilers. This will require ammonia injection, such as in selective catalytic reduction (SCR), in many power plants, resulting in ammonia deposition on fly ash. The presence of ammonia could create a barrier to fly ash utilization in concrete because of odor concerns. Although there have been limited studies of ammonia emission from concrete, little is known about the quantity of ammonia emitted during mixing and curing, and the kinetics of ammonia release. This is manifested as widely varying opinions within the concrete and ash marketing industry regarding the maximum acceptable levels of ammonia in fly ash. Therefore, practical guidelines for using ammoniated fly ash are needed in advance of the installation of many more SCR systems.

Conclusion

Ammonia release from mortar and concrete during mixing, placement, and curing was measured. Short-term levels in the air were found to be noticeable; however longterm effects were minimal. Work initially focused on laboratory mortar experiments to develop fundamental data on ammonia diffusion characteristics. Larger-scale laboratory experiments were then conducted to study ammonia emission from concrete containing ammoniated fly ash. The final phase comprised monitoring ammonia emissions from large concrete slabs. The data indicated that only 10 - 20% of the initial ammonia diffused from the concrete during 30-40 minutes of mixing, depending on the mix proportions and batch size. When placing concrete in an enclosed space, with negligible ventilation, it is recommended that the ammonia concentration in the concrete mix water should not exceed 110 mg NH_3/L, if the NIOSH exposure limit of 25 ppm in the air is not to be exceeded. If even a modicum of ventilation is present, then the maximum ammonia concentration in the concrete water would be approximately 170 mg/L. Long-term experiments indicated that ammonia diffusion from concrete was relatively slow, with greater than 50% of the initial ammonia content remaining in a concrete slab after 1 month. In general, during the mixing and placement of ammonia-laden concrete, no safety concerns were encountered. After one to two days, the ammonia level decreases to a point where it cannot be smelled. The only location where the ammonia concentration attained high levels (i.e. > 25 ppm in the air) was within the concrete mixing drum.

These findings are being distributed throughout the industry. The other project participants represent some of the country's largest ash marketers and a major utility; and will include these recommendations during interactions with cement companies. It is further hoped that the information will be used to adopt standards for use of ammoniated fly ash.