BIOGEOCHEMICAL REMEDIATION OF AMMONIA DISCHARGES FROM POWER PLANTS

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INTRODUCTION

Electric utilities often use a process of Selective Catalytic Reduction to reduce NOx emissions by reacting the NOx with ammonia. There is inevitably a small amount of unreacted ammonia in the wastewater. It is necessary to eliminate this ammonia loading before it discharges into rivers at levels that might be toxic to fish. During warm weather, nitrifying bacteria indigenous to the ponds appear to adequately accomplish ammonia detoxification (analogous to the nitrifying bacteria that control ammonia levels in an aquarium). However, these indigenous bacteria become relatively inactive in cold weather, leading to an increase in the level of ammonia being released into waterways constituting a significant concern to power plant operators and regulators. It is well known that in both freshwater and marine aquaria, a healthy nitrogen cycle operates; otherwise, rising levels of ammonia (from the animal wastes) would kill the fish and adversely impact the aquatic ecosystem.

GOALS AND EXPERIMENTAL APPROACH

The purpose of this project is to develop processes to mitigate ammonia discharges from ash ponds and related aqueous streams associated with ammonia inputs from coal use. The ammonia issue arises from implementation of the Selective Catalytic Reduction (SCR) process that removes NOx and SOx from flue effluents. With the advent of SCR's an ammonia stream is used as the electron donor meaning that excess ammonia is then discharged to fly ash ponds at concentrations of several ppm. The need for this research is because power plant effluents of even 1 ppm can rapidly kill fish in streams. Our research is focusing on ammonia pollution streams at an ammonia test facility, FoSCR Pilot Ponds at Tennessee Valley Authority's Paradise Fossil Plant in Kentucky. This research is closely linked with TVA and their Paradise generation plant. After several meetings with TVA personnel, a shared literature review and a review of previous TVA data we embarked on a field endeavor to track ammonia during the testing of ammonia discharges at the Paradise plant. Fly ashes and water samples at different locations in the fly ash pond 1, 3, and 50 ft from the fly ash slurry inputs at Paradise Fossil Plant were obtained to characterize water chemistry, fly ash mineralogy, chemical speciation and mass balances of ammonia in waters and solids prior to ammonia additions and post ammonia additions. Bench-scale studies have also been performed to develop strategies of ammonia removal and carbon sequestration using fly ash collected from the two pilot ponds at Paradise fossil plant.

TECHNIICAL PROGRESS

In FY 2002 Lauf and Phelps participated in a sampling event at the Paradise plant, near Crystal City, KY. Samples were retrieved by TVA at test ponds (Fig. 1) and made available for ORNL testing. Current testing is for biogeochemical parameters, chemical speciation and mass balances of waters and solids prior to ammonia additions, post ammonia additions and basin samples at different locations in the flay ash pond 1, 3, and 50 ft from the fly ash slurry inputs.

Fig. 1. Aerial photograph showing fly ash ponds and test ponds at Paradise Power Plant.

RESULTS

Analytical methods of determining fixed ammonium in fly ash sediments was developed and examined to ascertain a mass balance of ammonia. This is imperative for an understanding of ammonia removal mechanisms in fly ash ponds and would greatly complement TVA efforts as they have yet to account for the ammonia.

Table 1 shows chemical analysis of NH_4-N in fly ash slurry and fly ash pond water. To quantify NH_4-N concentration in fly ash sediment, KCl (2M) was used to extract NH_4-N from fly ash slurry (10 mL extractant/1 g of fly ash). The extraction method described involves equilibrium extraction in which the fly ash samples were extracted with an accurately measured volume of extractant for a specified time. After filtration using Whatman no. 42 filter paper, enough NaOH was added to extract and to keep

Table 1. Geochemical analysis of HN_4, total N, total C and pH of fly ash slurry and fly ash pond water from Paradise fossil plant ponds

Sample	Fly Ash Slurry					Fly Ash Pond Water	
	Total C (%)	**Total N (%)**	**KCl (2M) Extractable NH_4-N (ppb)**	**Hot water (90°C) Extractable NH_4-N (ppb)**	**HCl (1M) Extractable NH_4-N (ppb)**	**pH**	**NH_4-N (ppb)**
Sediment FGD Unit 2 End of Sluice Pipe	1.52	BD*	**5,810**	**4,856**	**6,314**	7.6	**100**
Sediment Upstream of NH_4 injection	1.15	0.008	**3,630**	**4,163**	**6,441**	10.9	**632**
Sediment Pond 1 Ash Delta	0.49	BD	**3,180**	**6,317**	**5,809**	12.2	**2,440**
Sediment Pond 1 Bottom Sediment	2.06	0.013	**3,685**	**5,064**	**4,416**	11.9	**1,571**
Water Pond 1 Water Station A	ND#	ND	**ND**	**ND**	**ND**	8.9	**927**
Sediment Pond 2 Surface Sediment	0.46	BD	**3,480**	**4,945**	**5,845**	ND#	**3,278**
Sediment Pond 2 Dike	0.71	0.002	**4,563**	**3,892**	**7,354**	ND	**1,807**
Water Pond 2 Water Station A	ND	ND	**ND**	**ND**	**ND**	8.9	**1,340**

*BD, Below detection limit.
#ND, Not determined.

pH 11.5 to 12.0. Indophenol Blue Method (Bremner, 1996) was use to analyze NH_3-N in the extractant using infrared spectroscopy. The limitation of sensitivity is 0.1 ppm.

XRD analysis of fly ash sampled at various points in ponds showed that major minerals are quartz (SiO_2), mullite ($3Al_2O_3{\cdot}2SiO_2$), silicon (Si), magnetite (Fe_3O_4), hematite (Fe_2O_3), and gypsum ($CaSO_4{\cdot}2H_2O$) (Table 2).

Bench-scale studies have been performed to develop strategies for ammonia removal and carbon sequestration using fly ash collected from the two pilot ponds at Paradise fossil plant. Fly ash collected at two points (Pond 1 bottom sediment and Pond 2 dike) in ponds were reacted with CO_2 (pCO_2 = 100%) and with N_2 in the presence of NH_4 (~105 ppm), 1 g of fly ash slurry with reacted with 15 mL deionized water containing NH_4 (~105 ppm) in a closed system using 26 mL anaerobic tubes. The headspace volume was 10 mL. Figure 2 shows that ammonia was sequestered into the fly ash under N_2 and CO_2 headspace.

These experiments indicate that fly ash slurry from Paradise Steam Power plant has NH_4 sequestration capacity of 68–111 mg NH_4/kg (8.5 to 13.3 % of total NH4 in the system) ash slurry under N_2 atmosphere and 82–116 mg NH_4/kg (10 to 13.9 % NH_4 in the system) ash slurry under CO_2

Table 2. Mineralogical analysis of fly ash slurry sediments used for bench-scale carbon sequestration and ammonia removal study

Sample	Mineralogy	
	Fly Ash Slurry from Paradise Plant	**Fly Ash Slurry from Paradise Plant (After reacting with 120 mM $NaHCO_3$)**
Sediment FGD Unit 2 End of Sluice Pipe	Gypsum ($CaSO_4 \cdot 2H_2O$)	Calcite ($CaCO_3$), Bassanite ($CaSO_4 \bullet 0.5\ H_2O$)
Sediment Upstream of NH_4 injection	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)	Quartz (SiO_2), Calcite ($CaCO_3$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)
Sediment Pond 1 Ash Delta	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)	Quartz (SiO_2), Calcite ($CaCO_3$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)
Sediment Pond 1 Bottom Sediment	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)	Quartz (SiO_2), Calcite ($CaCO_3$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)
Sediment Pond 2 Surface Sediment	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)	Quartz (SiO_2), Calcite ($CaCO_3$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)
Sediment Pond 2 Dike	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)	Quartz (SiO_2), Calcite ($CaCO_3$), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite (Fe_3O_4), hematite (Fe_2O_3)

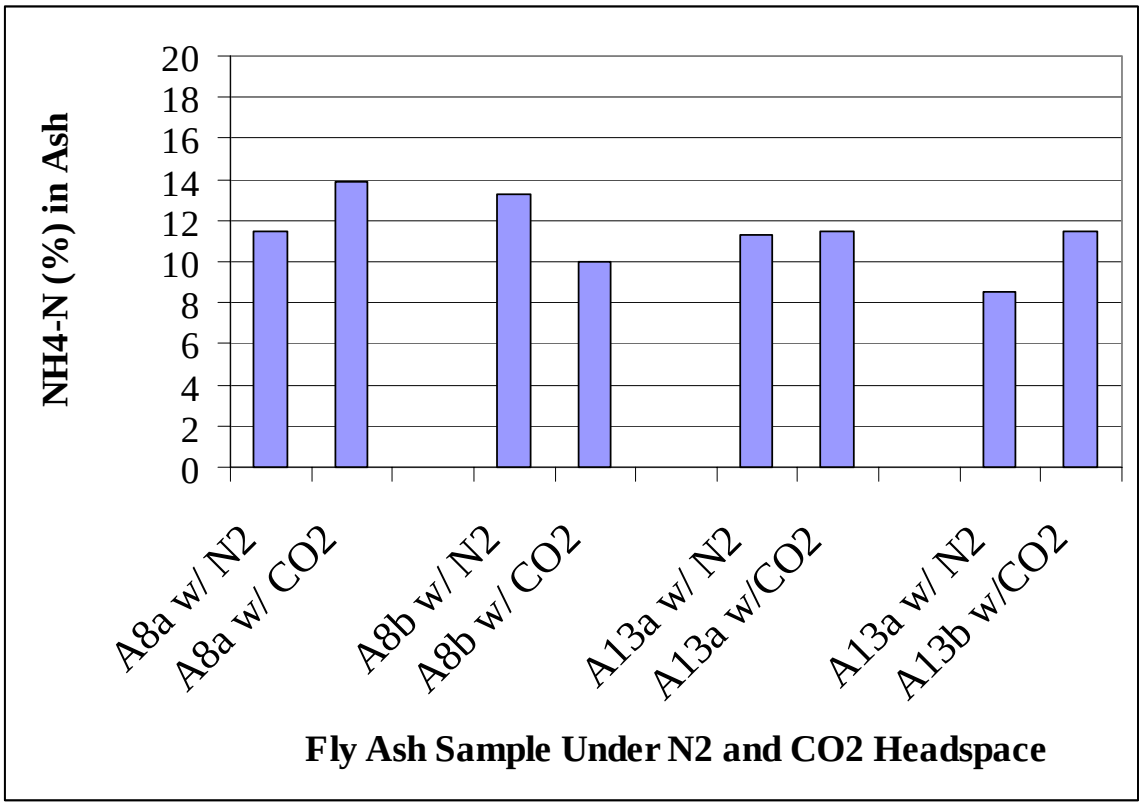

Fig. 2. Ammonia sequestered into fly ash sample obtained from Paradise plant under N_2 and CO_2 atmosphere.

atmosphere, likely sufficient to mitigate ammonia discharges from the ponds if that sequestration capacity were approached.

XRD analysis of ash sampled after reacting with CO_2 and NH_4 showed that increased pCO_2 (210 mM HCO_3^-) facilitated carbonate mineral (calcite, $CaCO_3$) formation (Table 3). Ammonia, to some extent, is also expected to be sequestered in carbonate minerals.

Table 3. Mineralogical analysis of fly ash slurry sediments used for bench-scale carbon sequestration and ammonia removal study

Sample	Mineralogy	
	Fly Ash Slurry from Paradise Plant	**Fly Ash Slurry from Paradise Plant (After reacting with 120 mM $NaHCO_3$)**
Sediment FGD Unit 2 End of Sluice Pipe	Gypsum ($CaSO_4 \cdot 2H_2O$)	**Calcite ($CaCO_3$)**, Bassanite ($CaSO_4 \bullet 0.5\ H_2O$)
Sediment Upstream of NH_4 injection	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)	Quartz (SiO_2), **Calcite ($CaCO_3$)**, Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)
Sediment Pond 1 Ash Delta	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)	Quartz (SiO_2), **Calcite ($CaCO_3$)**, Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)
Sediment Pond 1 Bottom Sediment	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)	Quartz (SiO_2), **Calcite ($CaCO_3$)**, Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)
Sediment Pond 2 Surface Sediment	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)	Quartz (SiO_2), **Calcite ($CaCO_3$)**, Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)
Sediment Pond 2 Dike	Quartz (SiO_2), Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)	Quartz (SiO_2), **Calcite ($CaCO_3$)**, Mullite ($3Al_2O_3 \cdot 2SiO_2$), Silicon (Si), Magnetite(Fe_3O_4), hematite(Fe_2O_3)

IMPLICATIONS

Ammonia content of the pond water samples indicated that ammonia is likely being removed and/or (co)precipitated within feet and after minutes of entering the fly ash ponds. Effluents from the FGD sluice pipe are diluted ~1:6 with fly ash. Upstream of the ammonia and in the FGD effluent the ammonia concentration is far less than 1 ppm. After the 2 ppm ammonia injection both pond 1 and pond 2 waters exhibit 2–3 ppm ammonia. However, within feet of distance and minutes of travel time more than one half of the ammonia is lost within the system, likely bound in the sediments. By the time waters reached sampling station A in both ponds ~2/3 of the ammonia was lost within the system. Attempts to account for the ammonia in the sediments have not been sufficient to close a mass balance as the sediments represent less than a two percent slurry of solids. TVA data concurs that they are accounting for less than 25% of the ammonia in mass balances. While it is convenient to suggest that the lost ammonia is due to

biology, the fact that it occurred during cold climates within days of the restart of ammonia injection further heightens our speculation that ammonia is lost within the system. Chemical composition of the pond water and ash sediments indicated that Si, Al, Fe, Mg, Na, and other metals in the pond water are precipitated with fly ash sediments. The ammonia added to the pond water may be precipitated with these metals in the fly ash sediments.

FUTURE RESEARCH

Bench-scale studies are being performed to develop strategies of ammonia removal and carbon sequestration via biogeochemical processes using fly ash collected from the ponds at Paradise fossil plant. Analytical method for determining fixed ammonium in fly ash sediments is currently developing to ascertain a mass balance of ammonia. This would greatly complement TVA efforts as they have yet to account for the ammonia. Further bench-scale study may include biological components and/or may focus more on engineering aspects for enhanced geochemical removal/sequestration. Close collaborations with TVA will be important.

In collaborations with TVA we will pursue completing a mass balance for ammonia additions/losses from fly ash systems, far better than the current 20–50%. Importantly, we will scrutinize the impacts of ash, time, distance and flux of ammonia in the fly ash processing pond systems using closed headspace laboratory tests and relate to field studies.

ABSTRACTED PRESENTATION

Roh, Y., R. J. Lauf, and T. J. Phelps. “Utilization of Biomineralization Processes for Carbon Sequestration.” Oak Ridge National Laboratory. Environmental Sciences Division Carbon Management Seminar Series, October 2002, Oak Ridge, Tennessee.