

BIOGEOCHEMICAL REMEDIATION OF AMMONIA DISCHARGES FROM POWER PLANTS

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ABSTRACT

This study seeks and develops technologies for low-temperature biogeochemical pathways to establish a healthy ammonia detoxification system in fly ash ponds during months when low ambient temperatures prevent existing mesophilic bacteria from adequately converting ammonia to nitrate. This project intends to leverage the DOE-FE investment by collaborating closely with TVA and making use of TVA's power plants, ash ponds and source of ammonia inputs for collaborative upscaling experiments for ammonia detoxification. 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.

INTRODUCTION

Electric utilities often use a process of Selective Catalytic Reduction (SCR) to reduce NO_x emissions by reacting the NO_x 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.

EXPERIMENTAL APPROACH

The ammonia issue arises from implementation of the Selective Catalytic Reduction (SCR) process that removes NO_x and SO_x 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, Paradise, KY. Fly ash 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.

RESULTS

COMPLETE DEVELOPMENT OF FREE AND FIXED AMMONIA ANALYTIC PROCEDURES IN ASH SOLIDS. An analytical method of determining free and fixed ammonium in fly ash sediments was developed and examined to ascertain a mass balance of ammonia. This was 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. 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 fly ash test ponds (pond 1 and 3) and 50 ft from the fly ash slurry inputs.

Table 1 shows chemical analysis of NH₄-N in fly ash slurry and fly ash pond water. To quantify fixed ammonium in fly ash, we developed more stringent ammonia extraction procedures such as hot water (90°C) extractable NH₄-N and KCl (2 M) extractable NH₄-N in fly ash slurry extraction using wet samples. Chemical analysis of KCl (2 M) extractable ammonium-N and hot water (90°C) extractable ammonium-N in pond water indicated better recovery of the ammonia with our recently developed HCl extraction procedure. To quantify free ammonium in the head space, ammonia in the headspace was sampled using a 1 mL syringe and then dissolved the gas phase was placed into high pH distilled water (pH = 11, with addition of NaOH). To quantify free ammonium in the water in the fly ash slurry, the water was filtered using 0.45 µm filter and the

pH was increased up to 11 with NaOH. The dissolved ammonia in the high pH water from headspace and water was analyzed to quantify free ammonia in the water and headspace. 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 $\text{NH}_4\text{-N}$ (ppb)	Hot water (90°C) Extractable $\text{NH}_4\text{-N}$ (ppb)	HCl (1M) Extract -able $\text{NH}_4\text{-N}$ (ppb)	pH	$\text{NH}_4\text{-N}$ (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	0.01	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	2.06	0.01	3,685	5,064	4,416	11.9	1,571
Sediment Water Pond 1- Water Station A	ND [#]	ND	ND	ND	ND	8.9	927
Sediment Pond 2- Surface	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

CHARACTERIZATION OF FLY ASH MINERALOGY. XRD analysis of fly ash sampled at various points in ponds showed that major minerals are quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), silicon(Si), magnetite(Fe_3O_4), hematite (Fe_2O_3), and gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Table 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 ·2H ₂ O)	Calcite (CaCO ₃), Bassanite (CaSO ₄ ·0.5 H ₂ O)
Sediment Upstream of NH ₄ injection	Quartz(SiO ₂), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)	Quartz(SiO ₂), Calcite(CaCO ₃), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)
Sediment Pond 1–Ash Delta	Quartz(SiO ₂), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)	Quartz (SiO ₂), Calcite(CaCO ₃), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)
Sediment Pond 1 Bottom	Quartz(SiO ₂), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)	Quartz(SiO ₂), Calcite(CaCO ₃), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)
Sediment Pond 2-Surface	Quartz(SiO ₂), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)	Quartz(SiO ₂), Calcite(CaCO ₃), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)
Sediment Pond 2-Dike	Quartz(SiO ₂), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)	Quartz(SiO ₂), Calcite(CaCO ₃), Mullite(3Al ₂ O ₃ ·2SiO ₂) Silicon(Si), Magnetite(Fe ₃ O ₄), hematite(Fe ₂ O ₃)

SCALE-UP STUDY TO QUANTIFY AMMONIA IN ASH SLURRY, WATER AND HEADSPACE DURING AMMONIA REMOVAL. 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 CO₂ (pCO₂ = 100%) and with N₂ in the presence of NH₄ (~105 ppm) in 160 mL serum bottles or 5 g of fly ash slurry reacted with 200 mL deionized water containing NH₄ (~105 ppm) in a closed system using 500 mL serum bottles (Figure 1).

Quantification of ammonia sequestered into the fly ash under N₂ and CO₂ headspace indicated that fly ash slurry from Paradise Steam Power plant has an NH₄ sequestration capacity of 68 – 111 mg NH₄/kg (8.5 to 13.3 % of total NH₄ in the system) ash slurry under N₂ atmosphere and 82 – 116 mg NH₄/kg (10 to 13.9 % NH₄ in the system) ash slurry under CO₂ atmosphere. This is likely sufficient to mitigate ammonia discharges from the ponds so long as that sequestration capacity were not approached.

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 were diluted ~1:6 with fly ash. Upstream of the ammonia and in the FGD effluent the ammonia concentration was 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 was 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 2 % 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 geochemically reacted and bound to the sediments 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 methods for determining fixed ammonium in fly ash sediments are 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 studies may include biogeochemical 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.



Figure 1. Scale-up ammonia sequestration experiment using sand (left, control) and fly ash from Paradise power (Center and Right) to quantify free and fixed ammonia.

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