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Guidelines for Integrated Management of Multiple Constituents in Ash Ponds—Volume 1

Technical Report

Guidelines for Integrated Management of Multiple Constituents in Ash Ponds—Volume 1

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PRODUCT DESCRIPTION

This document is a guidance manual that power plants can use to help better manage their ash ponds to comply with wastewater regulations. This first volume of this manual will focus on three of the commonly regulated parameters; total suspended solids (TSS), pH, and ammonia.

Results & Findings

This manual will help coal-fired power plants understand how to manage the operation of ash ponds to control discharge of ammonia, TSS, and pH. Case studies discussing practices currently being implemented at operating plants are presented to help understand the mechanisms by which ammonia is removed from ash ponds and what can be done to enhance those mechanisms.

Challenges & Objectives

The objectives of this manual are to:

- To assist coal-fired power plants in understanding the existing and future regulatory issues that may affect their discharge of ammonia, TSS, and pH
- To identify factors that may impact the ability to meet existing and future discharge limits for these parameters
- To identify the sources of these parameters within the facility
- To discuss practices currently being used to manage the operation of ash ponds to control these parameters.

Applications, Values & Use

As regulations, operations practices, and pollution control technologies change over time, this document will aid facilities in determining how to best manage their ash ponds to adapt to these changes.

Volume I is focused on ammonia, TSS, and pH. Additional volumes will be published as necessary to stay up to date with changes in the regulations, plant operation, and control technologies for other parameters.

EPRI Perspective

Ash pond management is becoming more challenging as time passes. Increased environmental controls for air emissions are resulting in significant changes to pond inputs. Ammonium, mercury, selenium, and other constituents are all expected to increase. EPRI’s goal is to develop guidance for integrated management that will maximize the pond’s ability to function as a treatment system as well as an ash deposition system. Ecological processes will be exploited to reduce the need for additional treatment systems such as metals removal or treatment for nutrients. This report will be updated annually for the next several years.

Approach

The information contained in this manual is based on the personal experience of the investigators, previous studies, and ongoing studies at coal-fired power plants.

Keywords

Ash pond
pond management
Ammonia
TSS
pH
Nitrification
Algal assimilation

ABSTRACT

This document is a guidance manual that power plants can use to help better manage their ash ponds to comply with wastewater regulations. This first volume of this manual will focus on three of the commonly regulated parameters; TSS, pH, and ammonia. The purpose of this manual is to:

1. Assist facilities in understanding the existing and future regulatory issues that may affect their discharge of these parameters;
2. Identify plant operating factors that may impact the ability of the facility to meet existing and future discharge limits for these parameters;
3. Identify the sources of these parameters within the facility; and
4. Discuss practices used to manage the operation of ash ponds to control these parameters, including case studies of current practices being implemented by operating plants.

As regulations, operations practices, and pollution control technologies change over the years, this document will also need to evolve and should not be considered a static document. Future updates and additional volumes of this document will be published as necessary to stay up-to-date with changes in the regulations, plant operation, and control technologies.

ACRONYMS AND ABBREVIATIONS

°C	Degrees Celsius
°F	Degrees Fahrenheit
µm	Micrometer
AOB	Ammonia Oxidizing Bacteria
C	Carbon
CFR	Code of Federal Regulations
cm	Centimeter
CWA	Clean Water Act
DO	Dissolved Oxygen
ELS	Early Life Stages
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator
ft	Foot
FGD	Flue Gas Desulfurization
fpm	Feet Per Minute
FR	Federal Register
H	Hydrogen
H^+	Hydrogen Ion
hp	Horsepower
H_2SO_4	Sulfuric Acid
HRT	Hydraulic Retention Time
lbs	Pounds
mg	Milligram
mg L^{-1}	Milligrams Per Liter
mgd	Million Gallons Per Day
mm	Millimeters
N	Nitrogen
NH_3	Un-Ionized Ammonia

NH_4^+	Ammonium Ion
NO	Nitrogen Oxide
NO_x	Nitrogen Oxides
NOB	Nitrate Oxidizing Bacteria
NPDES	National Pollutant Discharge Elimination System
O	Oxygen
O&G	Oil and Grease
P	Phosphorus
PCB	Polychlorinated Biphenyl
PISCES	Power Plant Integrated Systems-Chemical Emissions Study
POTW	Publicly Owned Treatment Works
ppmv	Parts Per Million by Volume
ppmw	Parts Per Million by Weight
SCR	Selective Catalytic Reduction
S.G.	Specific Gravity
SIP	State Implementation Plan
SNCR	Selective Non-Catalytic Reduction
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
SU	Standard Units
TN	Total Nitrogen
TP	Total Phosphorus
TRI	Toxics Release Inventory
TSS	Total Suspended Solids
USEPA	U.S. Environmental Protection Agency
WET	Whole Effluent Toxicity
WQC	Water Quality Criteria

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INTRODUCTION

Introduction

Historically, ash ponds at steam electric power plants have been primarily designed, operated, and managed to provide sufficient area and volume for sedimentation and long-term storage of the ash and to meet historical categorical effluent limitations for pH and total suspended solids (TSS). The locations of the ash ponds were selected to provide as much ash storage as possible with little consideration for future changes in wastewater regulations and requirements.

As wastewater regulations have changed and evolved throughout the years, the concept that ash ponds are simply a hole in the ground for storing ash is no longer applicable. New, pending, and future regulations will require that existing ash ponds be actively operated and managed to achieve new discharge limits set by the regulations. When new ash ponds are needed for either a new power plant or to meet the needs of an existing power plant, the design and construction of the new pond(s) must take into account the need for treatment of the water to remove parameter other than TSS, i.e., ash.

This document has been developed as a guidance manual that coal-fired power plants can use to help better manage their ash ponds to comply with wastewater regulations. Since regulations, plant operations, and pollution control technologies will continue to evolve, this document will also evolve and should not be considered a static document. Future updates and additional volumes of this document will be published as necessary to stay up-to-date with changes in the regulations, plant operations, and control technologies.

This first volume of this manual will focus on three of the commonly regulated parameters; ammonia, TSS, and pH. The purpose of this manual is to:

1. Assist facilities in understanding the existing and future regulatory issues that may affect their discharge of these parameters;
2. Identify plant operating factors that may impact the ability of the facility to meet existing and future discharge limits for these parameters;
3. Identify the sources of these parameters within the facility; and
4. Discuss practices used to manage the operation of ash ponds to control these parameters, including case studies of current practices being implemented by operating plants.

Current and Potential Regulatory Issues

The following sections discuss the current and potential regulatory issues that affect or may potentially affect discharges from ash ponds. These discussions will focus on the regulatory issues for ammonia, TSS, and pH, since they are the parameters of concern for this volume.

Categorical Standards

Under Title III of the Clean Water Act (CWA), the U.S. Environmental Protection Agency (USEPA) sets effluent guidelines for wastewater discharges to surface waters and publicly owned treatment works (POTWs). These effluent guidelines are national standards for existing sources and new sources from specific classes or categories of industries and activities, typically referred to as categorical standards. The effluent limits are technology-based (i.e., they are based on the performance of treatment and control technologies), and are written into the National Pollutant Discharge Elimination System (NPDES) permit for facilities in the class or category. Steam electric power generation plants (henceforth referred to as generation plants) are subject to a categorical standard defined in 40 CFR 423.

The categorical standard for generation plants sets the effluent limitations based upon the source of the discharge and whether the source is new or existing. The effluent limitations established for discharges of fly ash and bottom ash transport water are summarized in Table 1-1. All generation plants must meet these limitations for discharges from fly ash and bottom ash ponds to be in compliance with the categorical standards. Stricter limits can be set by states and local regulators.

Table 1-1
Categorical Standards for Fly Ash and Bottom Ash Pond Discharges

Parameter	Units	Monthly Average	Monthly Maximum
Total suspended solids (TSS)	mg L^{-1}	30.0	100.0
Oil and grease (O&G)	mg L^{-1}	15.0	20.0
pH	SU	6.0 – 9.0	6.0 – 9.0
Polychlorinated biphenyls (PCBs)	mg L^{-1}	No discharge allowed	No discharge allowed

Note:
mg L^{-1} = milligrams per liter; SU = standard units

Categorical standards are reviewed and updated. The USEPA began a detailed study of the Steam Electric Power Generation point source category in the 2005 annual review. It is expected that in late-2006 the USEPA will publish their strategy for this categorical standard.

Ammonia Limitations

Under the Clean Water Act, USEPA is required to publish and periodically update ambient water quality criteria (WQC). Ammonia is included as part of the ambient WQC in order to protect aquatic life. An update to the water quality criteria for ammonia, containing USEPA's most recent freshwater aquatic life criteria, was published in 1999.

The new criteria reflect recent research and data since the original water quality criteria for ammonia, first published in 1984, and are a revision of several elements of the 1984 criteria, including the pH and temperature relationship of the acute and chronic criteria and the averaging period of the chronic criterion. As a result of these revisions, the chronic criterion is now dependent on pH, temperature, and the presence or absence of sensitive life stages. The acute criterion for ammonia is dependent on pH and fish species.

The new ammonia in-stream criteria are designed to protect early life stages (ELS) of sensitive aquatic species. These limits are more stringent with increasing pH, and also are likely to be lower during the early spring when temperatures are colder. Colder operating temperatures will reduce ammonia removal and may result in increased regulatory risk if stringent discharge limits are imposed. Effluent toxicity also may be an issue at higher ammonia concentrations and/or higher discharge pH.

Nutrient Limitations

Since 2000 USEPA has announced the publication of recommended water quality criteria for nutrients under section 304(a) of the Clean Water Act (see 66 FR 1671) for 26 of 29 areas identified by USEPA, which USEPA terms ecoregions. Nutrient criteria are numerical values for both causative (phosphorus and nitrogen) and response (chlorophyll a and turbidity) variables associated with the prevention and assessment of eutrophic conditions. States and tribes are expected to adopt or revise the ecoregional nutrient criteria into water quality standards. These nutrient water quality criteria may result in the addition of limitations for phosphorus and nitrogen to the discharge permits of coal-fired power plants.

Effluent Toxicity

On July 7, 1994, USEPA issued a national policy on effluent limitations in NPDES permits to control whole effluent toxicity (WET) for the protection of aquatic life. The policy stated that NPDES authorities (regions, states, and tribes) must determine whether a discharge causes, has the reasonable potential to cause, or contributes to an in-stream excursion above a numeric criterion or a narrative criterion within an applicable state water quality standard and, where appropriate, establish permit limits on WET, for lethal and sub-lethal effects.

The term WET is used to describe the aggregate toxic effect of an aqueous sample (e.g., whole effluent wastewater discharge) as measured by an organism's response to exposure to the sample (e.g., lethality, impaired growth or reproduction). WET test methods are established to replicate, to the greatest extent possible, the total effect and actual environmental exposure of aquatic life to toxic pollutants in an effluent.

Ammonia in ash pond discharges can potentially pose a toxicity issue. In water, ammonia can be present as either un-ionized ammonia (NH_3) or ammonium ion (NH_4^+). Un-ionized ammonia is more toxic to aquatic organisms than ammonium ion. Therefore, the fractions of NH_3 and NH_4^+ are of importance when considering the toxicity of a discharge. The individual fractions in the water depend on the pH of the water, as shown in Equation 1-1.

$$NH_3 + H^+ \leftrightarrow NH_4^+ \qquad \textbf{Equation 1-1}$$

As the pH of the water increases, the proportion of NH_3 will increase and, conversely, as the pH decreases, the proportion of NH_3 will decrease. Therefore, even without a discharge limit on ammonia, the amount of ammonia discharge may need to be limited in order to meet WET requirements. At a pH of 9.3 the concentrations of NH_3 and NH_4 are approximately equal. Below this pH, NH_3 (toxicity) decreases rapidly and the allowable concentration of total ammonia increases 10-fold for each unit change in pH.

Plant Operating Practices that Could Lead to Ash Pond Wastewater Issues

Coal–fired steam electric power plants typically use ash ponds for treatment of the various wastewaters generated in the plant. Each of these wastewater streams contributes various amounts and types of pollutants to ash ponds. The most common sources of ammonia, TSS, and contaminants that affect pH are briefly described below, with a more detailed description of each contained in subsequent sections of the manual.

Ash sluicing is typically the largest source of TSS, and can be a significant source of ammonia, if selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) systems are used for removal of nitrogen oxides (NO_X). Ash sluicing also can contribute either alkalinity or acidity, resulting in an increase or decrease of pH depending on the type of coal being used. Coals with a high calcium and low sulfur content produce alkaline fly ash and low calcium high sulfur content coals tend to produce acidic fly ash. Ash sluicing can contribute ammonia as well if ash conditioning for electrostatic precipitator (ESP) enhancement is done. Ash conditioning can reduce the pH of the wastewater stream depending on the chemical used for conditioning. Ammonia conditioning of the ash will contribute ammonia and reduce the pH due to the production of sulfuric acid (H_2SO_4). Mitigation of SO_3 using ammonia will both contribute ammonia and reduce the pH due to the production of H_2SO_4.

Conditioning with sulfur trioxide (SO_3) will produce H_2SO_4, causing a reduction in pH.

Purge streams for flue gas desulfurization (FGD) systems will produce a high TSS concentration waste stream, if the stream is not treated prior to entering the ash pond.

Regeneration of demineralizers will result in swings in pH, since the regeneration process requires both acid and hydroxide to regenerate the demineralizer media.

Coal pile and pyrite pile runoff will both result in highly acidic water due to the oxidation of the pyrite.

Equipment cleaning results in a wastewater stream with a low pH, due to removal of fly ash that has accumulated in the corners and crevices of the equipment.

2

AMMONIA

Sources of Ammonia in Ash Ponds

Ammonia may be used for several different purposes within a power plant. The primary area where it is used in significant quantities is within the air pollution control systems. The following sections will identify the potential systems where ammonia may be used and how the ammonia will make its way to the ash ponds.

Electrostatic Precipitator Ash Conditioning

ESPs are employed to remove fine particles (fly ash) from flue gas. The ESP works by generating a high-voltage electric field in an electrode located in the passage through which the flue gas flows. The electric field ionizes the gas molecules near the electrode. As the flue gas passes through the ESP, the ionized molecules collide with and attach to the fly ash and other fine particles, thus inducing a charge on the particles. The charged particles are attracted to (or precipitated on) a collector plate of the opposite charge as the particles. The particles are removed intermittently by rapping the collector plates, causing the collected particles to fall by gravity to a hopper in the bottom of the ESP.

The efficiency of an ESP is dependent on the temperature and chemistry of the flue gas and the composition of the particulate materials, all of which affect the electrical resistivity of the fly ash. Fly ash with lower electrical resistivities tends not to affect the efficiency of ESP. However, fly ash with higher electrical resistivities, generally greater than 10^{12} ohm·cm, are poorly removed by ESPs. At high resistivities, the current density and voltage of electric field between the electrode and collector plate decreases, potentially causing sparking, arc-overs, and other effects that reduce the efficiency of the ESP. In general, the resistivity of fly ash tends to increase with decreasing sulfur content of the coal and with increasing temperature.

Combustion of coal generates sulfur dioxide (SO_2) and SO_3. When exposed to water vapor, the sulfur trioxide forms H_2SO_4. The H_2SO_4 is adsorbed on the fly ash, which reduces the electrical resistivity of the fly ash and enhances ESP performance. However, the H_2SO_4 also lowers the pH of the sluice water stream, leading to increased solubilization of many metals. As power plants switch to low sulfur content coal to meet emission regulations for sulfur dioxide, the lower quantities of SO_3 result in lower quantities of H_2SO_4 available for adsorption on the fly ash, which will increase the resistivity. This higher resistivity can reduce the efficiency of the ESP.

In order to reduce the resistivity and maintain ESP performance, the fly ash particles may be chemically conditioned to reduce the resistivity. Different methods of chemically conditioning the fly ash have been used, including ammonia injection.

Ammonia is injected into the flue gas prior to the ESP to condition the fly ash. The mechanisms by which the ammonia reduces the electrical resistivity and/or improves the ESP efficiency depends upon the composition of the fly ash, and the temperature and composition of the flue gas. The major mechanisms that may be occurring include:

- The ammonia, SO_3, and water vapor react to create a thin conductive field on the surface of the flash particles, thus decreasing resistivity.
- The ammonia and SO_3 react to create fine particles of ammonium sulfate and the fine particles create a space-charge effect in the field, which increases the electrical field in the ESP and improves efficiency.
- The ammonia and SO_3 react to create ammonium bisulfate; at typical flue gas temperatures the ammonium bisulfate will be at or below its freezing point, resulting in a semi-liquid state; the semi-liquid state will increase agglomeration of the particles with fly ash, thus improving removal efficiency.

As these particles are collected on the collector plates and periodically removed, the ammonia is removed with the particles as they are collected in the hopper of the ESP. If the fly ash is removed by wet-sluicing, the ammonium bisulfate dissolves, adding soluble ammonia to the sluice water which is subsequently discharged to the ash pond.

Mitigation of SO_3

Production of SO_3 is becoming a greater concern in power plants due to the potential impacts on both plant emissions, and plant operation and maintenance. There are no environmental regulations for SO_3 in power plant emissions; however, the SO_3 can impact the air emissions. Depending on the temperature, water vapor content, and particulate content of the flue gas, the SO_3 in the flue gas will react with the moisture and particulates to produce H_2SO_4 aerosol, referred to as a “blue plume.” This aerosol will increase the opacity of the plant emissions and can result in a violation of opacity limits. Additionally, H_2SO_4 aerosol is reportable under the USEPA Toxics Release Inventory (TRI) program.

The H_2SO_4 can also cause issues with the operation and maintenance of the plant. When the flue gas temperature falls below the dew point of H_2SO_4, the H_2SO_4 condenses and collect on the surfaces of the plant equipment, resulting in corrosion and increased maintenance.

To mitigate the opacity problem and corrosion issues, ammonia is mixed with the SO_3 containing gas. The ammonia and SO_3 react to produce ammonium bisulfate, which forms a particle that is removed subsequently by the electrostatic precipitators along with the fly ash. When sluiced with water, the ammonium bisulfate dissociates, releasing ammonia and sulfuric acid to lower the pH of the sluice water, as shown in the equation below.

$$NH_4HSO_4 \rightarrow NH_4^+ + H^+ + SO_4^{-2} \qquad \textbf{Equation 2-1}$$

Selective Catalytic Reduction and Selective Non-Catalytic Reduction

Environmental regulations, based on the requirements of the Clean Air Act Amendments of 1990, have required states to develop state implementation plans (SIPs) to reduce airborne emissions of the six priority air pollutants (ozone, sulfur dioxide, carbon monoxide, nitrogen oxides, particulate matter and lead). The SIPs have been developed to help reduce emission of pollutants to meet goals in non-attainment areas. Non-attainment of ozone goals led the USEPA to request 22 states (mostly east of the Mississippi) to develop plans to reduce emissions and attain statewide NO_x emission targets. The electric utility industry has been a focus of this due to emissions of NO_x, which reacts with volatile organic carbons in the presence of sunlight to create "ground level" ozone. This effect is most pronounced during the "ozone season" from May 1 to September 30. Consequently, the electric utility industry is moving forward with implementing NO_x reduction measures during this "ozone season."

Two of the primary technologies currently being used at coal-fired electric power stations for reduction of NO_x emissions are SCR and SNCR. Both SCR and SNCR systems use ammonia to react with the nitric oxide (NO) and other nitrogen oxides in the flue gas to produce nitrogen gas (N_2) and water.

In SCR systems, the ammonia and flue gas mixture pass through a catalyst at 500°F to 650°F (260°C to 340°C) where the reaction takes place. In SNCR systems, the ammonia is injected into the flue gas on the hot-side of the boiler where the temperature is high enough to drive the reaction of ammonia with the NO_x to form N_2. The NO_x reduction efficiencies are approximately 80-90%, and 40-60% for SCR and SNCR systems, respectively.

The SCR and SNCR systems will generally feed an excess of ammonia to assure that stoichiometric requirements are meet, thus creating a "slip" of unreacted ammonia exiting in the flue gas stream. The ammonia slip for an SCR system can range from less than 1 part per million by volume (ppmv) to 20 ppmv. As the SCR catalyst ages, its activity decreases, and the ammonia slip increases. Typical ammonia slip values from operating SCR system are generally in the 0 to 2 ppmv range. The ammonia slip for SNCR systems is higher than with SCR systems, ranging from about 5 ppmv to greater than 25 ppmv. Typical ammonia slip values from operating SNCR facilities are generally in the 5 to 10 ppmv range.

The ammonia slip will be adsorbed by the fly ash in the flue gas. The use of SCR and SNCR systems may have a significant effect on wastewater management at power plants because of the potential release of ammonia into wastewater treatment systems. At typical ammonia slip values, concentrations of ammonia on dry fly ash range from less than 50 parts per million by weight (ppmw) to over 500 ppmw. When the fly ash is wet-sluiced, the adsorbed ammonia is released into the sluice water and subsequently discharged to the ash pond. If a fly ash with an ammonia concentration of 100 ppmw is wet-sluiced producing a slurry with 5% ash, the ammonia concentration in the sluice water will be 5 milligrams per liter (mg L^{-1}), assuming all ammonia is released to the water, and there is no volatilization of the ammonia.

Figure 2-1 illustrates the ammonia cycle at a typical coal-fired station using SCR and SNCR systems [1].

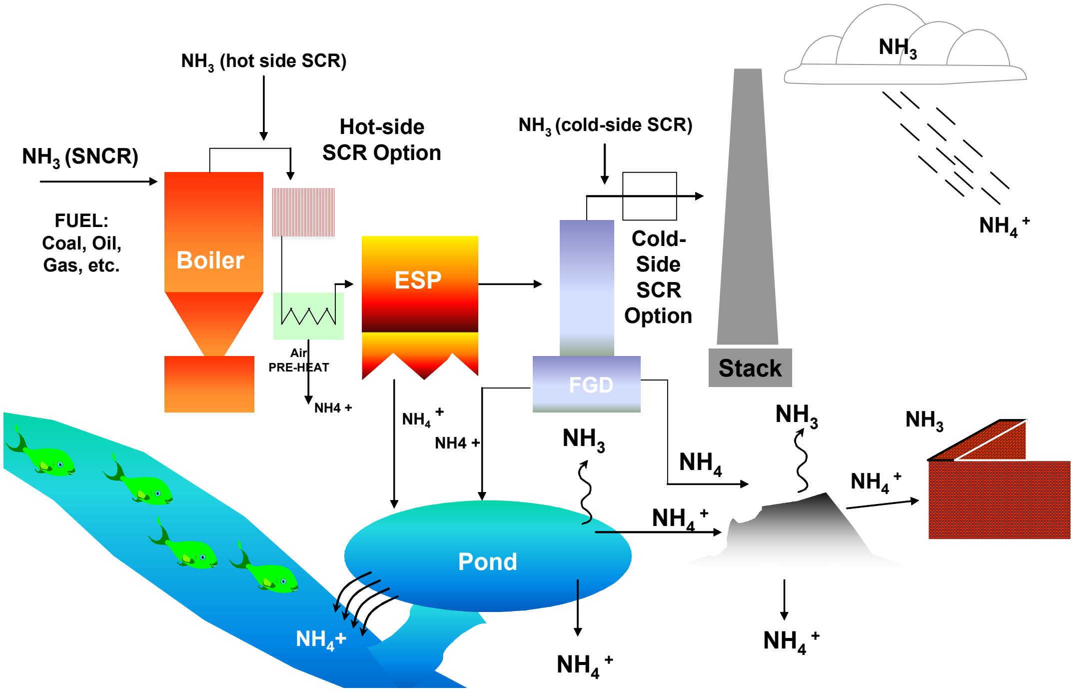

Figure 2-1
Ammonia Sources and Sinks Arising from ESP Conditioning, and Operation of SCR and SNCR

Flue Gas Desulfurization

Ammonia remaining after ash conditioning, SO_3 mitigation efforts, and SCR/SNCR systems will be absorbed in the scrubber liquor of the FGD systems. Research has shown that approximately 90% of the ammonia entering the FGD will be absorbed in the scrubber liquor. A portion of the scrubber liquor is regularly removed (blowdown) to maintain the desired conditions in the scrubber. The blowdown is either sent to a dewatering system or to a waste pond, where the solids are separated from the blowdown stream. The water from the blowdown stream, with the ammonia, will potentially be discharged to the ash ponds, resulting in a higher ammonia concentration in the ash pond.

Fate of Ammonia in Ash Ponds

Ammonia discharged to ash ponds may be removed from the wastewater (i.e., fly ash sluice water, FGD waste pond effluent) via the several mechanisms. These include the following:

- Algal assimilation
- Bacterial oxidation of ammonia (nitrification)
- Uptake by wetland plants
- Volatilization (little removal expected)
- Settling by association with solids (little removal expected)

Each of these mechanisms is discussed below.

Algal Assimilation

All organisms, whether algae, bacteria, plants, or animals, are primarily made up of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and phosphorus (P), with small fractions of other elements. A typical algal cell is assumed to have a chemical composition of $C_{106}H_{263}O_{110}N_{16}P$, which, on a dry mass basis, is approximately 36% C, 7.4% H, 50% O, 6% N, and 1% P.

In the presence of sunlight, algae use carbon dioxide, water, and sunlight to synthesize their own food (glucose) and oxygen, instead of eating other organisms or relying on material derived from them. This process is called photosynthesis and the general equation for it is:

$$6H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 \text{ (glucose)} + 6O_2 \qquad \textbf{Equation 2-2}$$

The glucose is then used to produce other organic compounds needed by the cells for growth, and used as a fuel for other cellular functions. When used, the glucose and other compounds react to produce chemical energy, carbon dioxide and water. This process is called respiration and is described by the following equation:

$$C_6H_{12}O_6 \text{ (glucose)} + 6O_2 \rightarrow \text{energy} + 6CO_2 + 6H_2O \qquad \textbf{Equation 2-3}$$

Both photosynthesis and respiration occur during daylight, with only respiration occurring after daylight. The rate of photosynthesis far exceeds the respiration rate resulting in a net increase of oxygen during the daylight. A net consumption of oxygen will occur during the night. The excess oxygen produced during the daylight will be expelled from the cell as a byproduct and can result in supersaturation of the water with oxygen during day. At night, when oxygen is being consumed, the dissolved oxygen (DO) will be depressed below the saturation point. The rates at which photosynthesis and respiration processes take place are dependent on several factors, including sunlight intensity, sunlight duration, nutrient concentration, and temperature. As each of the factors increase, the rate of production of new algal mass will be higher. Under these conditions, algal blooms can occur in ash ponds with long residence times. Algal blooms can produce hypoxic (low oxygen) or anoxic (no oxygen) conditions in the pond, potentially killing the algae, strictly aerobic bacteria, and fish. Algae die-off can lead to release of ammonia from decaying algae.

During the photosynthesis and respiration processes, the algae will also absorb N, P, and other trace nutrients needed to build new cell matter and sustain cell functions. Based on the typical composition of algae, $C_{106}H_{263}O_{110}N_{16}P$, 6.3 mg L^{-1} of NH_3-N (and 0.9 mg L^{-1} of P) are required to produce 100 mg L^{-1} of new algal mass, or approximately 15.9 pounds (lbs) of algae per 1.0 lbs of NH_3-N. Ammonia is the easiest form of nitrogen for uptake and assimilation by algae and it will be preferentially consumed from the water column for production of new biomass, with nitrate being preferred next. Several factors influence ammonia uptake, including temperature, concentrations of other essential nutrients, available DO, and presence of inhibitory substances. While manipulation of these parameters is well understood in municipal wastewater treatment applications, operating ash ponds with low organic loadings for removal of ammonia is not a common treatment practice. Successful operation of ash ponds as ammonia treatment processes will likely require site-specific understanding of the pond's process microbiology.

Growth of algae will also have on impact on the pH of the ash pond. As discussed above, the algae remove CO_2 from the water during daylight (photosynthesis) and release CO_2 back to the water during nighttime (respiration). The change in CO_2 throughout the day will change the carbonate equilibrium in the pond. Consumption of CO_2 will tend to decrease the hydrogen ion (H^+) concentration in the water to maintain the carbonate equilibrium, causing an increase of the pH of the water. Conversely, release of CO_2 will tend to increase the H^+ concentration in the water, causing a decrease of the pH of the water. This cycle of photosynthesis during the day and respiration at night will create a diurnal pattern in the pond pH. The degree to which the pH will change is dependent on several factors, including the initial pH, the alkalinity, and the available nutrients in the water. This change may be significant enough to potentially violate pH discharge limits (typically limits require pH to be between 6.0 and 9.0, specified in the categorical standard) – especially the higher pH range. Growth of algae will also have an impact on TSS in the pond.

Bacterial Oxidation of Ammonia (Nitrification)

Certain bacteria use ammonia solely as their energy source. This process is called nitrification and is the conversion of ammonia-nitrogen to nitrate-nitrogen. The conversion occurs in two steps, with each step being mediated by different genera of bacteria. The first step involves the conversion of ammonium to nitrite which is mediated by ammonia oxidizing bacteria (AOB—historically considered to only be the genus *Nitrosomonas* but now recognized to potentially represent a wider range of ammonia oxidizing bacteria). The second step is the conversion of nitrite to nitrate, which is mediated by nitrate oxidizing bacteria (NOB – historically considered to only be the genus *Nitrobacter* but now recognized to potentially represent a wider range of nitrate oxidizing bacteria). The chemical reactions for these steps are provided below.

$$2\ NH_4^+ + 3\ O_2 + \textit{Nitrosomonas} \rightarrow 4\ H^+ + H_2O + 2\ NO_2^-$$ **Equation 2-4**

$$2\ NO_2^- + O_2 + \textit{Nitrobacter} \rightarrow 2\ NO_3^-$$ **Equation 2-5**

These two steps result in an overall nitrification reaction given by the following equation:

$$NH_4^+ + 2\ O_2 \rightarrow 2\ H^+ + H_2O + NO_3^-$$ **Equation 2-6**

Using this equation we can calculate the theoretical oxygen requirement for nitrification. Two moles of O_2 are required to oxidize 1 mole of NH_4^+-N. On a mass basis, this is equivalent to 4.57 lbs of O_2 to oxidize 1.0 lbs of NH_4^+-N.

Simultaneously with nitrification, the bacteria use the energy, ammonium, oxygen, inorganic carbon, and other nutrients to generate new cell mass. The generation of new cell matter (assumed to be $C_5H_7O_2N$) is given by the following general chemical equation.

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- \rightarrow$$

$$0.021\ C_5H_7O_2N + 0.98\ NO_3^- + 1.041\ H_2O + 1.88\ H_2CO_3$$ **Equation 2-7**

Based on this equation, the theoretical inorganic carbon requirements for production of new cell mass can be determined. The bacteria will need 1.98 moles of HCO_3^- to convert 1 mole of NH_4^+-N into 0.021 moles of new cell mass. On a mass basis, this is equivalent to 7.14 lbs of alkalinity (as $CaCO_3$) required to oxidize 1.0 lbs of NH_4^+-N. The equation also indicates that 0.17 lbs of new cell mass will be produced per 1.0 lbs of NH_4^+-N removed. The 0.17 lbs of new cell mass will be composed of both *Nitrosomonas* and *Nitrobacter* bacteria, with 0.15 lbs being *Nitrosomonas* and 0.02 lbs being *Nitrobacter*. As compared to assimilation of NH_4^+-N by algae, nitrification will produce significantly less solids (15.9 lbs of algae versus 0.17 lbs of bacteria per 1.0 lbs of NH_4^+-N removed). Therefore, if nitrification is used to remove the ammonia, rather than assimilation by algae, the amount of solids produced will be nearly 100 times less.

Initiation and maintenance of nitrification is dependent on the rate at which the nitrifying bacteria grow and reproduce. The rate at which the bacteria reproduce must be greater than the rate at which they are lost from the system through death or being washed out in the effluent. Studies have shown that the growth rate of *Nitrosomonas* is much less than the growth rate of *Nitrobacter*, and therefore is the controlling growth rate. The growth rate of *Nitrosomonas* is dependent on the temperature, NH_3-N concentration, and DO concentration. The growth rate for *Nitrosomonas* is given by the following equation:

$$\mu_T = \mu_{\max} \times \Theta^{T-25} \times \left(\frac{NH_4^+ - N}{K_N + NH_4^+ - N} \right) \times \left(\frac{DO}{1 + DO} \right)$$

Equation 2-8

Where:

$\mu_T = specific\ growth\ rate, d^{-1}$

$\mu_{\max} = maximum\ specific\ growth\ rate,\ 0.65\ d^{-1}$

$\Theta = temperature\ correction\ coefficient,\ 1.055$

$T = temperature,\ °C$

$NH_4^+ - N = concentration\ of\ NH_4^+ - N,\ mg/L$

$K_N = half - saturation\ constant\ for\ NH_4^+ - N,\ mg/L$

$DO = dissolved\ oyxgen\ concentration,\ mg/L.$

In order to maintain a sufficient nitrifying bacteria population, the hydraulic retention time (HRT) of a pond must be greater than the inverse of the specific growth rate minus the decay rate, known as the doubling rate for the bacteria, otherwise the cells wash out of the ponds faster than they grow. This is represented by the following equation:

$$HRT \geq \frac{1}{\mu_T - k_d}$$

Equation 2-9

Where:

$$HRT = \frac{Volume\ of\ Pond}{Influent\ Flow\ to\ Pond},\ d$$

$$k_d = decay\ rate = 0.05 \times \Theta^{T-25},\ d^{-1}.$$

Figure 2-2 shows the minimum HRT or doubling rate required for nitrification to prevent wash-out of the nitrifying bacteria as a function of temperature. The HRT must be greater than the doubling rate of the nitrifying bacteria in order to replenish those that have been carried out in the effluent of the pond. The figure assumes a NH_4^+-N concentration of 1 mg L^{-1}, and DO concentration of 2 mg L^{-1}.

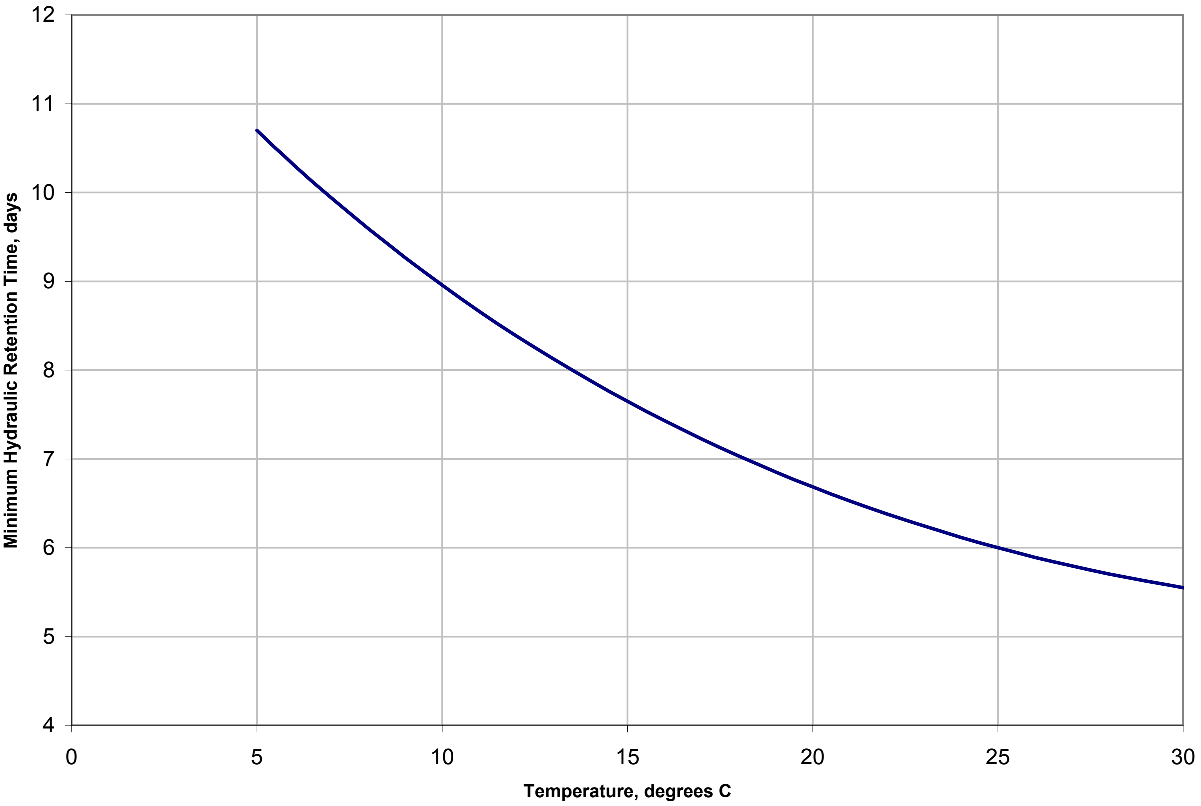

Figure 2-2
Minimum Hydraulic Retention Time (Nitrifier Doubling Rates) to Prevent Wash-Out of Nitrifying Bacteria

Under ideal conditions, at pond temperatures of 5°C, 15°C, and 25°C, the nitrification doubling rate and the HRT required to be able to retain a sufficient quantity of nitrifying bacteria to maintain nitrification are10.7 days, 7.6 days, and 6.0 days, respectively. Typically, there are other factors that affect the doubling rate (e.g., pH less than ideal, low DO) and the actual doubling rate is longer, so the ideal doubling rate is multiplied by a safety factor of at least 1.5 in order to assure that nitrification will be maintained. These values assume that the pond is well mixed so that the nitrifying bacteria and influent ammonia are well mixed and distributed throughout the pond, that the nitrifying bacteria are fully suspended in the water column, and that the system is operating under long-term, steady-state conditions.

However, ash ponds do not operate under long-term, steady-state conditions. Seasonal variation in the amount of ammonia discharged to ash ponds because of seasonal operation of SCRs and SNCRs result in very low levels of nitrification in the spring. When little or no ammonia has been discharged to the ash pond over the winter, the inventory of nitrifying bacteria will be low because of limited food source (ammonia) and the cold temperature, which slows the growth of the bacteria to a point where they cannot keep up with washout. When the loading of ammonia to the pond suddenly increases due to ammonia slip, the limited inventory of the bacteria is not sufficient to consume all of the ammonia. There needs to be growth of 0.17 lbs/day of nitrifying bacteria for each pound of ammonia per day nitrified. If the doubling rate of nitrifiers is 20 days due to the low temperature, less than ideal pH, and/or other factors, then there needs to be 20 times 0.17 or 3.4 pounds of nitrifiers to nitrify each pound per day of NH_3-N. It is not unusual for ponds to receive 400 lbs/day of NH_3-N. This will require a nitrifying population of 1,360 lbs. Later in the summer, when the doubling rate is 4 days, then the required bacterial inventory drops to 272 lbs. Sometime between spring and summer as the pond temperature increases, the growth rate increases sufficiently to achieve the decreasing requirement for bacterial population to nitrify the incoming ammonia. This results in poor ammonia removal in the spring with rapidly increasing capacity for nitrification throughout the summer.

As discussed above, nitrification requires DO. In ash ponds, the primary sources of DO are from surface reaeration and photosynthesis by algae. Surface reaeration and photosynthesis generally keep the upper layer of the pond well oxygenated during daylight. However, during nighttime, respiration by algae can significantly reduce the DO concentration, even down to zero. Without sufficient DO, the nitrifying bacteria will not reproduce (so this volume cannot be “counted” in the required volume – as described above). In order to maintain a sufficient DO concentration, an additional source of oxygenation, such as installation of surface aerators, may be required.

In addition to C, H, N, and O, the nitrifying bacteria require other nutrients and trace elements. Beyond C, H, N, and O, the next nutrient needed in the highest amount is P. The P requirement for bacteria is 0.8 lbs per 100 lbs of bacteria. Therefore, for an influent ammonia concentration of 10 mg L^{-1}, 0.14 lbs P per 1.0 lbs of NH_3-N is required.

For other trace elements, each 1.0 mg of nitrifying bacteria requires the quantity listed in Table 2-1 [4].

Assuming an influent NH_3-N concentration of 10 mg L^{-1}, one would produce 1.7 mg L^{-1} of nitrifying bacteria to nitrify this amount. The concentrations of nutrients (other than the NH_3-N and DO that are converted to nitrite and nitrate) needed for growth of new nitrifying bacteria are listed in Table 2-2.

In contrast, algae would require approximately 81 times these requirements, based on a yield of 15.9 lbs of algae for the same amount of NH_3-N removal.

Table 2-1
Trace Element Requirements per 1 mg of Nitrifying Bacteria

Constituent	Mass (mg)
N	0.05
P	0.01
K	0.006
Ca	0.006
Mg	0.004
S	0.004
Na	0.001
Cl	0.001
Fe	0.001
Zn	0.0001
Mn	0.0001
Cu	0.00001
Mo	0.000002
Co	0.0000002

Table 2-2
Comparison of Trace Element Requirements for Nitrification and Algal Uptake of 10 mg/L of NH_3-N

Constituent	Concentration (mg L^{-1})	
	Required for Nitrification	Required for Algal Assimilation
K	0.010	0.8
Ca	0.010	0.8
Mg	0.007	0.55
S	0.007	0.55
Na	0.0028	0.23
Cl	0.0028	0.23
Fe	0.0023	0.19
Zn	0.0002	0.02
Mn	0.0001	0.008
Cu	0.00002	0.002
Mo	0.000005	0.0004
Co	0.0000005	0.00004

Impacts of Pond Stratification

Most ash ponds are deep enough to go through a process of thermal stratification. Thermal stratification occurs because of the difference in density between warm and cold water. The density of water is at its highest at 4°C. At temperatures above 4°C, the density decreases as the temperature rises, and below 4°C, the density decreases as the temperature decreases. When there is a significant difference in the temperature profile in a pond, thermal stratification is likely to occur.

During the winter, a layer of colder water forms at the surface due to cold air temperature, and the pond is generally at the same temperature throughout the full depths with little mixing of the pond. In the early spring, as the ice melts away, the wind will begin to create circulation within the pond causing the contents of the pond to mix; this is generally called the spring overturn. Through the spring, the temperature of the upper layer of the pond will begin to increase as solar radiation and air temperature increase. The pond will begin to form three thermal layers:

- The epilimnion, which is the upper warm layer;
- The hypolimnion, which is the lower cold layer; and
- The metalimnion (or thermocline), which is the layer between with a large temperature gradient.

By mid-summer, the three layers will be fully developed. Wind will circulate the epilimnion causing the algae, nutrients, and DO to disperse throughout it’s shallow depth (e.g., 2-5m). The hypolimnion will be stagnant, generally with no DO present (i.e., anoxic), due to respiration by bacteria, algae, and other organisms, plus the isolation from inputs of new atmospheric oxygen. This condition will last until late fall, when temperature stratification breaks down. As the air temperature and solar radiation decrease in fall, the depth of the epilimnion will decrease until it eventually reaches a point where it begins to mix with the hypolimnion. When this happens, the pond will turn over again (fall overturn).

Stratification of the pond can lead to several undesirable conditions, such as:

- Short-circuiting of the flow through the pond;
- Nutrient (including ammonia) release; and
- Reduction in ammonia uptake.

Short-circuiting of the flow through the pond will occur in the summer because the epilimnion will act as a distinct layer in the pond, with no interaction with the lower hypolimnion. As the warm influent flow enters the pond, it will stay within the epilimnion, which is only a fraction of the total pond volume. This will result in a decrease in the actual HRT of the pond versus the theoretical HRT (total pond volume divided by the influent flow rate). Reduction in the HRT will reduce the time the ammonia is in contact with the algae and/or bacteria in the water, thereby reducing removal efficiency.

Nutrient release can occur when the hypolimnion is anoxic (no oxygen or nitrate). Deep thermally stratified ponds also can result in anoxic conditions [5]. The anoxic conditions will result in the death and decay of algae that have settled to the bottom of the pond, and release of ammonia and other nutrients that were previously assimilated for cell growth. These nutrients remain in the hypolimnion until the spring and fall overturns. During the overturns, the nutrients are mixed throughout the pond volume and can cause a sharp increase in the concentration of ammonia and other nutrients. Where discharge limits are placed on ammonia and other nutrients, this may result in violations of the limits.

In ponds where nitrification is occurring, the **reduction in HRT** will result in a much shorter time available to grow nitrifying bacteria, which may cause wash-out of the nitrifying bacteria. If the rate of wash-out is greater than the rate of production of nitrifiers for an extended period, then nitrification will be greatly reduced or may cease.

Anoxic conditions in the hypolimnion will also stop any nitrification by nitrifying bacteria that have settled and attached to the bottom of the pond (fixed-film nitrifiers). In ponds with large surface areas, nitrification by these fixed-film nitrifiers could be significant. Without this contribution, the reduction in ammonia may not be high enough to meet the discharge limits.

Uptake by Wetland Plants

Emergent wetland plants can remove ammonia from the water column during the growing season and may contribute ammonia during winter due to decay. A typical North American inland freshwater marsh will uptake an average of 0.001 pounds per square foot (lbs ft^{-2}) of ammonia annually [3]. As this is a yearly average, summer performance is likely to be substantially higher and winter performance substantially lower.

Natural ash sluice channels and the perimeter of ash ponds contain emergent wetland plants. However, the hydraulic loading rate in ash sluice channels is generally too high and the area along the perimeter of ash ponds is too low to promote any significant ammonia removal.

Volatilization

Aqueous ammonia is a pH-dependent equilibrium between gaseous ammonia molecules and ammonium ion. As shown in Figure 2-3, the equilibrium between ammonium ion and ammonia gas at 25°C favors higher concentrations of ammonia gas at a pH higher than 9.2, with significant concentrations at pH higher than 10. The equilibrium also shifts further towards ammonia gas as the temperature is increased. Under these conditions (i.e., high pH and high temperature), the ammonia gas can be released to the atmosphere, depending on the stripping action that the water stream containing the ammonia-laden water is exposed to. So, in well-mixed, high-pH waste streams, such as some high-pH fly ash sluice water streams, some ammonia gas can be volatilized. If this occurs, it has the potential to be a nuisance odor or worker safety issue. By contrast, under quiescent situations and lower pH and temperature found in ash ponds, little volatilization is likely. Because ash pond water is typically at less than pH 9, ammonium ion will predominate, and ammonia volatilization will not occur.

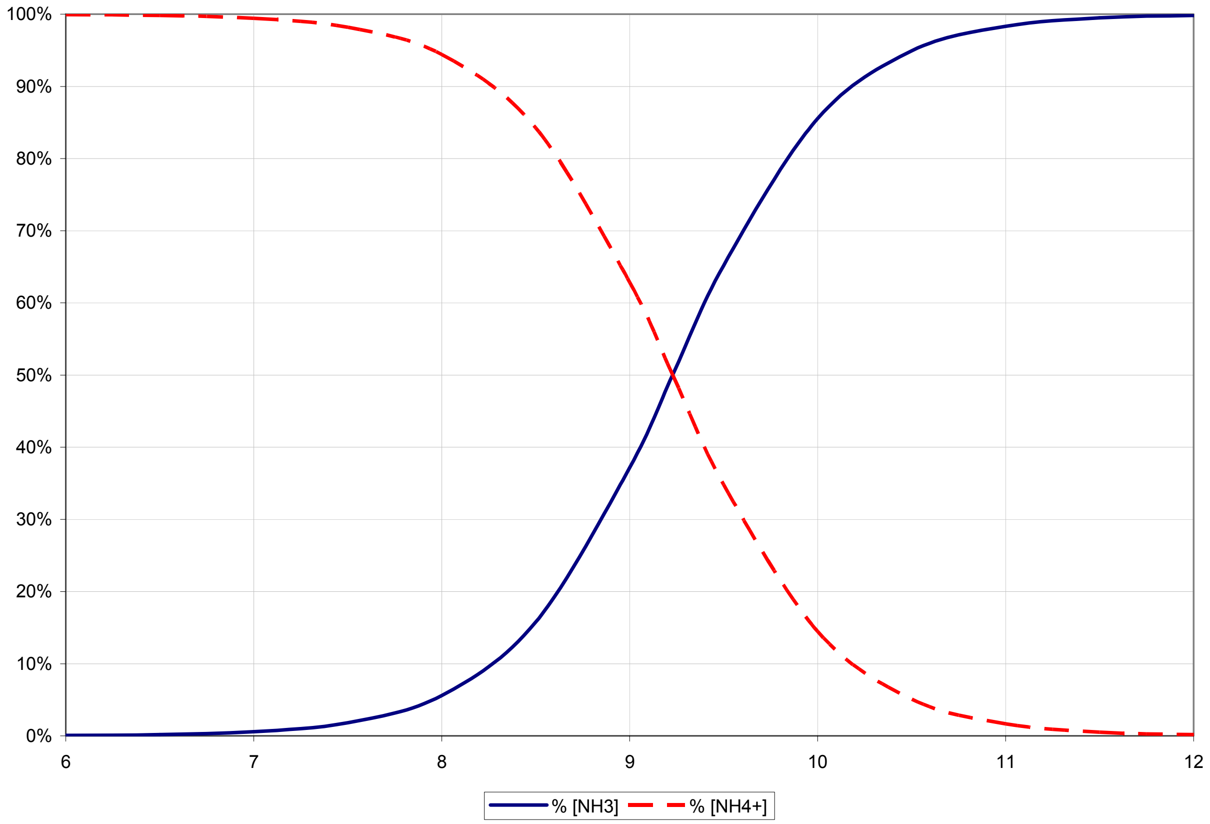

Figure 2-3
Ammonia Gas and Ammonium Ion Equilibria at 25°C

Ammonia is highly soluble in water, with a solubility of 529 g L^{-1}at 20°C. As such, when fly ash that has adsorbed ammonia is wet-sluiced, the ammonia will rapidly be released from the fly ash into the sluice water, and will not likely be adsorbed by other solids or be volatilized.

Settling by Association with Solids

Although ammonium ion can exhibit attraction to charged clay particle surfaces in the absence of other positive ions, it is not likely to associate with solid particles, such as fly ash, due to high solubility relative to other cations commonly found in high concentrations in power plant waste streams. Therefore, this is likely not a significant removal mechanism.

Ammonia Management Options

Due to existing or upcoming environmental regulations, electricity-generation companies have begun studying and/or implementing methods for managing ammonia in their existing ash ponds. Since ash ponds were originally intended for removal of solids from the sluice water and not ammonia removal, most ash ponds are simply water impoundments with a large surface area to allow for settling of the ash and a volume large enough to contain multiple years of ash. The pond design did not consider features needed to promote or enhance ammonia removal.

The primary methods available for ammonia management in existing ponds are algal assimilation and nitrification. Each of these methods requires active management of the pond to promote conditions to achieve them.

Ammonia management has been evaluated in other EPRI research projects as well [13, 14].

Eliminate Short-Circuiting/Maximize HRT

One of the first active management practices is to consider maximizing the actual HRT of and minimizing short-circuiting in the ash pond, since the effectiveness of removal mechanisms such as biological nitrification and algal assimilation are time-dependent. As discussed above, thermal stratification can significantly reduce the actual HRT, which reduces the volume available for treatment of the ammonia. Short-circuiting, caused by wind-driven currents, will also reduces the actual HRT and treatment.

Floating baffles are commonly used to increase the actual HRT. Partial-depth baffles, positioned perpendicular to the flow path, can be used to stop short-circuiting caused by wind-driven currents. An added benefit of partial-depth baffles is that they will help retain algae on the upstream side of the baffle. Depending on the position of the last baffle compared to the pond outlet, it can prevent discharge of algal blooms that may cause a violation of TSS limits.

Full depth baffles, with submerged flow-through ports below the epilimnion, can be used to promote vertical mixing, thus enhancing mixing between the epilimnion and the hypolimnion and increasing the actual HRT. Increased mixing, especially during the summertime when stratification is at its peak and DO concentration is at its lowest in the hypolimnion, will help reduce anoxic conditions in the hypolimnion, thus promoting nitrification throughout the full pond depth.

An alternative to the use of floating baffles is the use of floating mixers. Floating mixers can be used to circulate water from the surface down into the deeper depths of the pond. The circulating water will increase the actual HRT of the influent water and will carry DO deep into the pond, again promoting nitrification through the full pond depth. The mixing, however, will cause the algae to be moved out of the photic zone (i.e., the zone in which photosynthesis is occurring), thus reducing the assimilation of ammonia by algae.

Promote Algal Assimilation

Where algal assimilation is the method being used for management of ammonia, the key factor is to ensure that sufficient nutrients are available, so that growth of the algae is only limited by the available ammonia. After nitrogen from the assimilated ammonia, the next most important nutrient is phosphorus. A minimum theoretical nitrogen to phosphorus (N:P) mass ratio of 7.2 is required for growth; therefore, a ratio of less than this will not be limited by P. Assuming an ash pond influent ammonia concentration of 2 mg L^{-1} of NH_3-N, as a result of ammonia slip, the micronutrient and trace element requirements for assimilation by algae are listed in Table 2-2. Based on studies by EPRI [6, 7], it is likely that these requirements would be exceeded, although it is not known that the trace element concentrations in ash pond water are bioavailable to algae. The exception is P. The form of P available for use by the algae, orthophosphate, was not sufficient based on the type of coal used by the plant.

One consideration when using algal assimilation is the mass of algae produced. Assuming an influent ammonia concentration of 2 mg L^{-1} of NH3-N, with all other nutrients in sufficient quantities to not be limiting, approximately 32 mg L^{-1} of algae will likely be generated. The increase in algae concentration will result in higher TSS levels in the ash pond, and possibly the ash pond effluent. With a monthly average TSS discharge limit of 30 mg L^{-1} or less, as specified in the categorical standards, there is a higher potential of violating the TSS discharge limit.

Promote Nitrification

Nitrification has several advantages over algal assimilation, including:

1. Produces significantly lower cell mass yield (approximately 1% of algal assimilation), which results in less impact on effluent TSS
2. Occurs throughout the pond depth, whereas algae can only be produced in the photic zone

However, implementing and maintaining nitrification will require a high degree of active management of the ash pond conditions. Three factors are key to establishing reliable nitrification:

1. An HRT greater than the nitrifiers growth rate;
2. Adequate DO to meet the oxygen requirement of the nitrifiers; and
3. Alkalinity to replace that consumed by the nitrifiers.

As discussed above, the rate of nitrification depends on temperature. As the temperature decreases, the rate will decrease, and, conversely, as the temperature increases, the rate will increase. The design of nitrification processes are based on the minimum temperature of the water during the period when nitrification is to occur. Since the growth rate of the nitrifying bacteria is a function of the temperature of the water, the minimum temperature of the water during which nitrification is required must be used to determine the minimum HRT, as shown in Equations 2-8 and 2-9.

For example, if a power plant has a seasonal ammonia discharge limit from May 1 to October 31, the minimum ash pond temperature during that period will dictate the HRT required for achieving nitrification. If the actual HRT is less than the minimum HRT, then the nitrifiers will not grow fast enough to replenish those that have been washed out in the ash pond effluent. Assuming that the minimum pond temperature is 10°C, Figure 2-2 indicates that the minimum HRT required is 9.0 days. Typically, the actual HRT is multiplied by a safety factor of at least 1.5 to be certain that nitrifiers will not be washed out. Therefore, an HRT of at least 13.5 days would be recommended.

As described above in the Bacterial Oxidation of Ammonia (Nitrification) discussion, the sudden increase in ammonia fed to the pond in the spring can result in a sudden requirement for a large nitrifying bacterial population at a time when the growth rate is low. It takes 0.17 lbs of bacterial growth to nitrify a pound of ammonia. Lower growth rate requires more bacteria for the same load of ammonia. Low growth rate makes it harder to build the bacterial mass needed during this spring surge in ammonia.

Verification of a pond's actual HRT, through a tracer study, is recommended to determine if there is enough HRT. Studies conducted by EPRI member companies, have shown that the actual HRT can be significantly less then the theoretical HRT. For example, one study found that the actual HRT of the ash pond was from 1 to 7 days compared with a theoretical HRT of 20 days [8].

Nitrifiers require 4.57 lbs of oxygen per 1.0 lbs of NH3-N removed. Assuming an influent ammonia concentration of 2 mg L^{-1} of NH_3-N, a minimum of 9.1 mg L^{-1} of oxygen is needed. Depending on pond conditions, DO released by algae during photosynthesis can provide some or possibly all of that. However, the DO from photosynthesis will be depleted at night and will vary from day to day. Consequently, an external source of oxygen will likely be required.

For large treatment ponds, floating aerators are typically used for supplying oxygen. Floating aerators typically provide between 2.5 to 3.0 lbs of oxygen per hour per horsepower (hp). For an ash pond with an influent flow rate of 25 million gallons per day (mgd) and an influent ammonia concentration of 2 mg L^{-1} of NH_3-N, approximately 1,906 lbs/day of oxygen are needed. This would require approximately 27 to 32 hp.

An added benefit of floating aerators is that they provide significant mixing of the ponds. The mixing will:

- Increase the actual HRT by circulating stagnant or stratified areas in the zone of influence of the aerator
- Drive DO deeper into the pond depth providing oxygen to nitrifiers on the pond bottom
- Eliminate anoxic conditions on the bottom, eliminating the spring surge of ammonia release during overturn

Alkalinity is essential for nitrification to occur. Review of studies conducted by EPRI [6, 7] indicates that the alkalinity in ash pond influents is quite variable and may not meet the requirements for nitrification. In one study [7], the alkalinity ranged from 3 to 192 mg L^{-1} (as $CaCO_3$). At the lowest value, 3 mg L^{-1}, the theoretical ammonia removal by nitrification would be limited to 0.42 mg L^{-1}. Consequently, an alkalinity addition system will likely be required in many instances. The alkalinity addition system should be designed to provide the maximum demand for nitrification. For example, if an ash pond has a maximum influent flow rate of 30 mgd and a maximum influent ammonia concentration of 3 mg L^{-1} of NH_3-N, then the total alkalinity required would be 5,359 pounds per day or 14.3 mg L^{-1} (as $CaCO_3$).

Case Studies in Management of Ammonia in Ash Ponds

Case studies are presented below to demonstrate the approaches taken by two coal-fired power plants to identify the mechanism(s) by which ammonia is removed in operating ash ponds and what actions the plants have implemented to enhance those mechanisms.

Case Study #1 – Mass Balance Approach to Evaluating Fate of Ammonia in a Fly Ash Pond

A Midwestern coal-fired power plant uses ammonia for ash conditioning and for SO_3 mitigation. During the ozone season, these uses result in the fly ash pond having influent concentrations of NH_3-N in excess of 20 mg L^{-1}. In order to understand if the pond would remove the ammonia and the mechanisms by which the ammonia was removed, a mass balance approach was used to track the changes in ammonia, nitrite, nitrate, and alkalinity entering and exiting the pond.

The fly ash pond has a volume of approximately 237 million gallons. The average inflow of fly ash sluice water is 7 mgd, for a theoretical HRT of 34 days. Influent and effluent ammonia concentrations during the 2003 ozone season are shown as Figure 2-4.

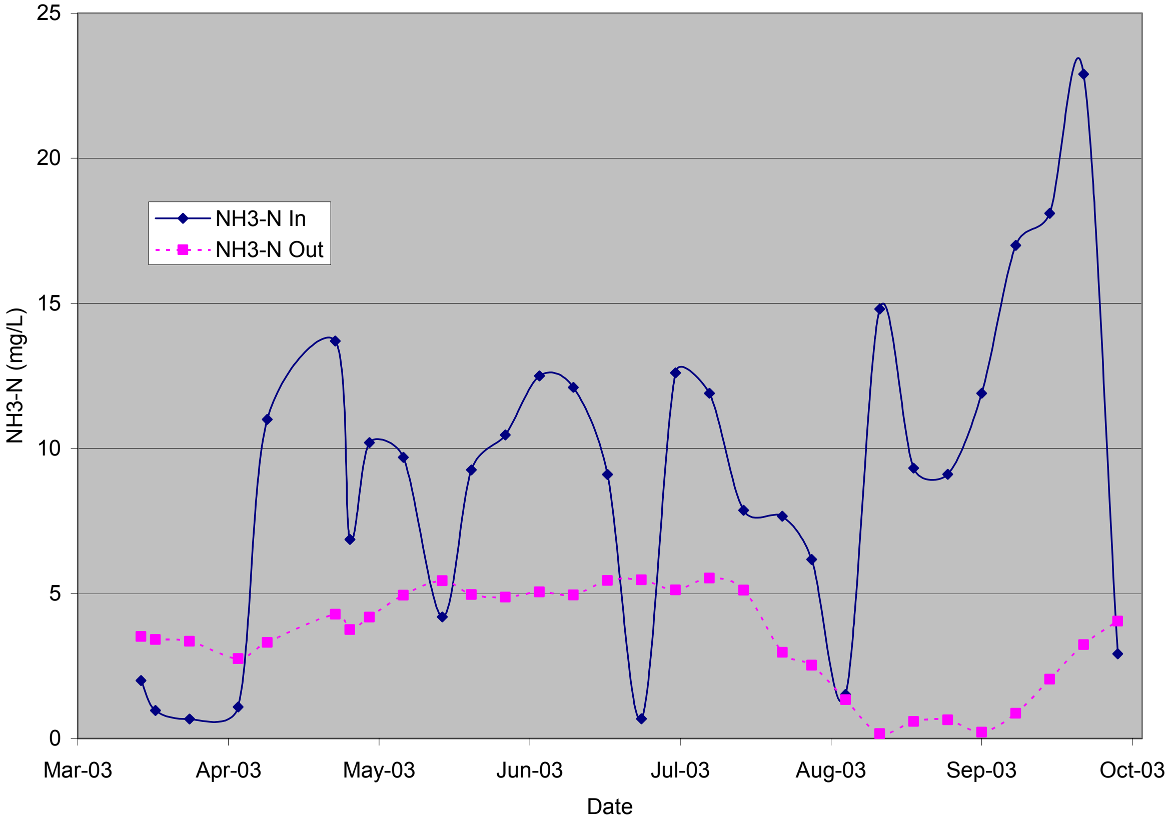

Figure 2-4
Influent and Effluent Ammonia Concentrations During the Ozone Season, 2003

This figure shows that the effluent concentration is typically less than the influent ammonia concentration. But there are times when the effluent is greater than the influent, which can be misleading when considering the data on a daily basis. Since the pond has such a long HRT (34 days), the peaks and valleys of the influent are dampened in the large volume. Therefore, the monthly average concentrations are more representative of the pond performance. Monthly average concentrations are shown in Figure 2-5.

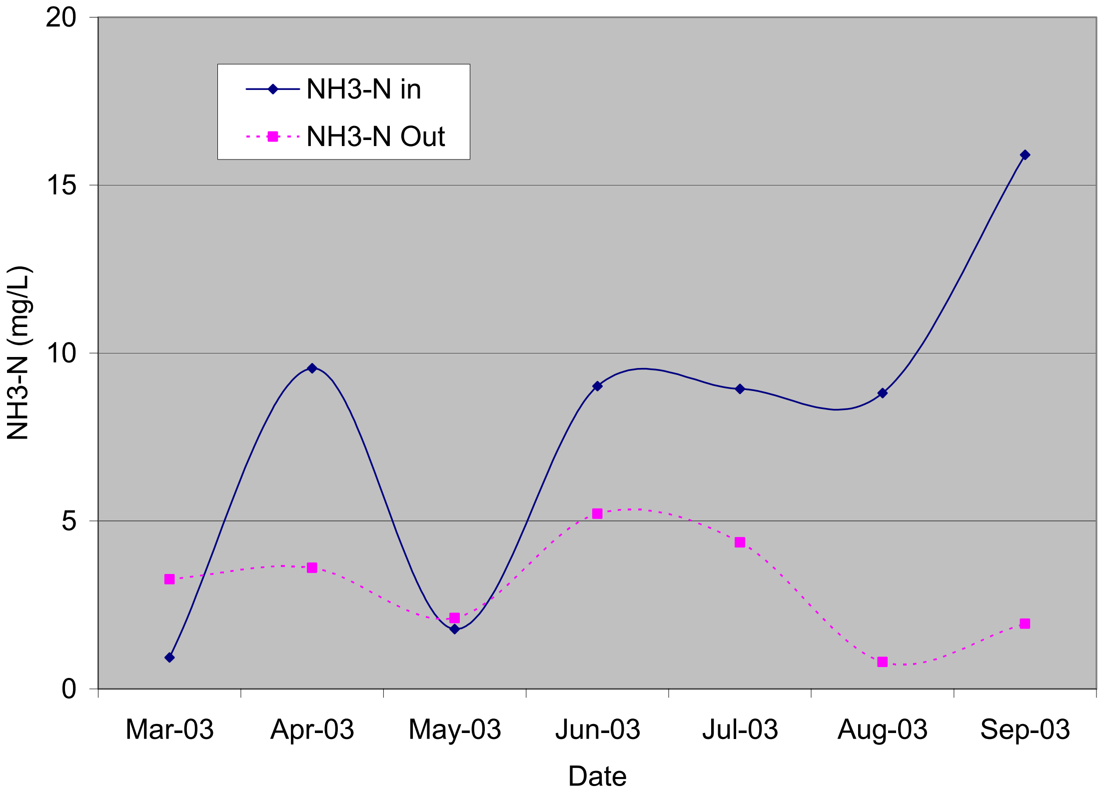

Figure 2-5
Monthly Average Influent and Effluent Ammonia During Ozone Season, 2003

A simple mass balance is illustrated by Figure 2-6.

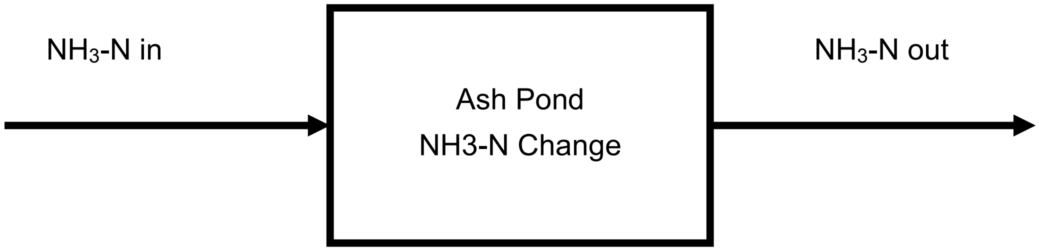

Figure 2-6
Mass Balance for Ammonia

If there is no destruction (or creation) of ammonia, the mass balance would be represented by Equation 2-10. Each of these rates would be shown as mass per unit time, in this case lbs/day.

NH_3-N Change = NH_3-N in - NH_3-N out **Equation 2-10**

Where the ammonia was reacted (by either nitrification or algal assimilation) the mass balance can be used to calculate the quantity lost by these processes, using Equation 2-11.

$NH3\text{-}N \text{ Reacted} = NH_3\text{-}N \text{ in} - NH_3\text{-}N \text{ out} - NH_3\text{-}N \text{ Change}$ **Equation 2-11**

The data for flows and concentrations of nitrogen species (specifically ammonia, and a combination of nitrite plus nitrate) in the influent, in the pond and in the effluent were used to perform daily mass balances of the two nitrogen species. Using Equations 2-12 through 2-14:

$NH_3\text{-}N \text{ in} = (NH_3\text{-}N \text{ in}) \times Q \times 8.34$ **Equation 2-12**

$NH_3\text{-}N \text{ out} = (NH_3\text{-}N \text{ out}) \times Q \times 8.34$ **Equation 2-13**

$NH_3\text{-}N \text{ change} = \{(NH_3\text{-}N \text{ in pond})_2 - (NH_3\text{-}N \text{ in pond})_1\} \times V \times 8.34$ **Equation 2-14**

Where:

$(NH3\text{-}N \text{ in})$ = concentration of ammonia in influent in mg L^{-1}

Q = flow into the pond in mgd

$(NH_3\text{-}N \text{ in pond})_1$ = concentration of ammonia in pond at day 1 in mg L^{-1}

$(NH_3\text{-}N \text{ in pond})_2$ = concentration of ammonia in pond at day 2 in mg L^{-1}

V = volume of pond in millions of gallons

A similar mass balance was performed on nitrite plus nitrate for the pond. The daily mass balances were averaged for each month and are shown as Figure 2-7. The apparent nitrogen loss during April and May is probably due to algal uptake since there is not an equivalent generation of nitrite and nitrate.

In June, there is an average of 300 lbs/day loss of NH_3-N and a 200 lbs/day increase in nitrite and nitrate. This is evidence of 200 lbs/day of NH_3-N being nitrified and the remaining 100 lbs/day being lost through some combination of nitrification/denitrification or algae uptake. In any event, the majority of the ammonia loss is due to nitrification. In July and August there is an increase in nitrification.

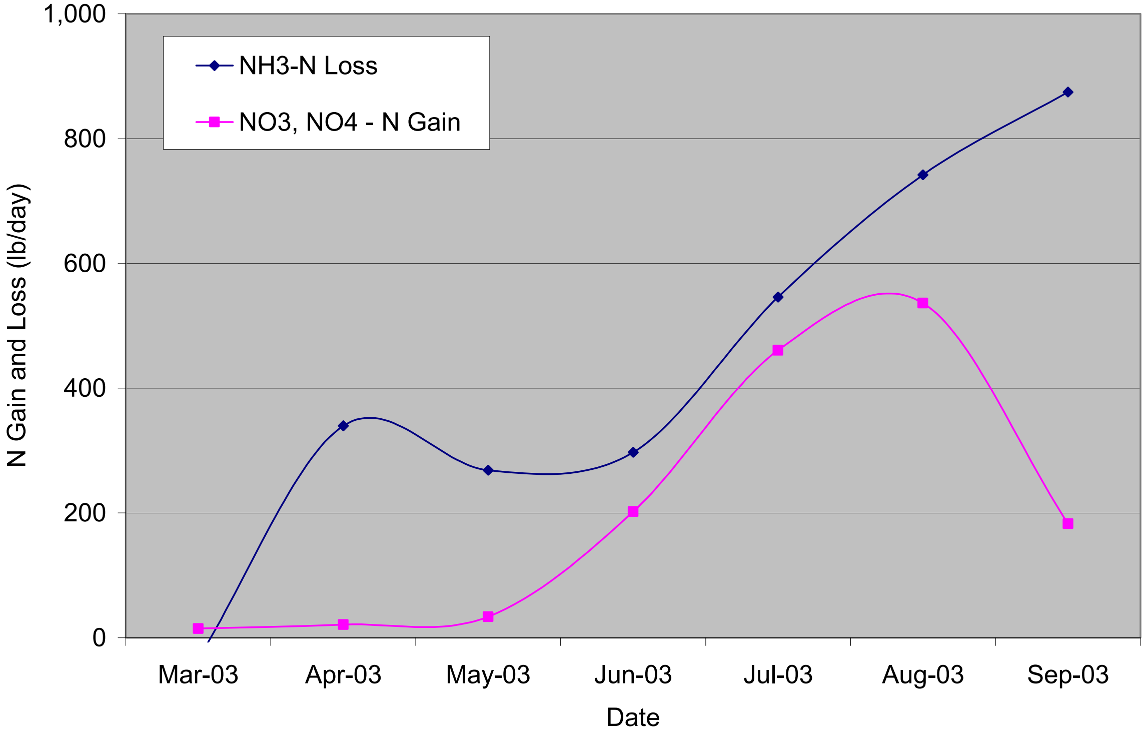

Figure 2-7
Monthly Average Nitrogen Mass Balance Season 2003

Figure 2-8 shows ammonia loss and nitrite plus nitrate gain data for 2003 through 2005. As can be seen, there was significantly greater removal of ammonia nitrogen in 2003 than in subsequent years. Where the nitrite plus nitrate gain is close to the ammonia loss, this indicates that nitrification is occurring. Where the ammonia loss is much different than the nitrite plus nitrate gain, it is likely that nitrification is occurring as well as algal uptake and/or nitrogen loss through denitrification.

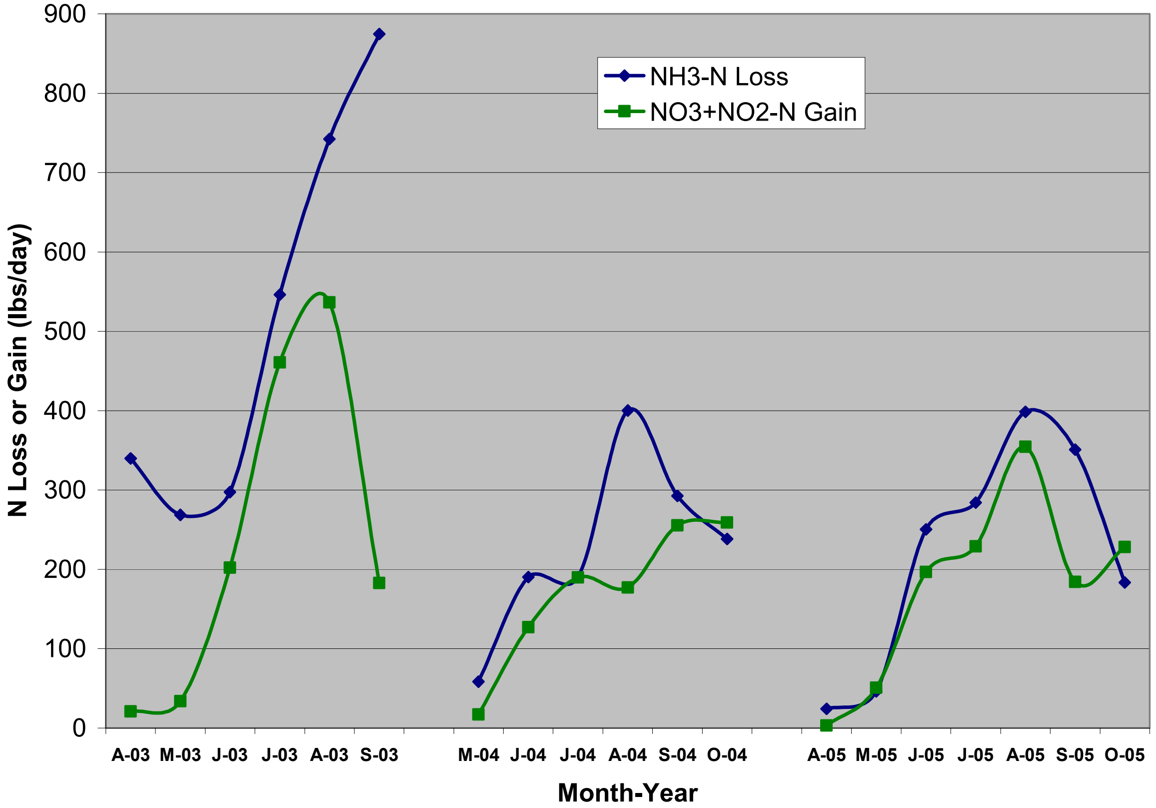

Figure 2-8
Monthly Average Nitrogen Mass Balance Season 2003 through 2005

Figure 2-9 shows the influent and effluent temperatures for the pond in 2003. The principal difference between the March through May period and the June through September period is temperature. The influent temperatures are much higher because this plant uses cooling tower blowdown for ash sluicing, and the ash itself imparts an elevated temperature to the ash sluice water. After this influent mixes with the pond water, the temperature is significantly reduced by the large volume of cooler water. Since the effluent from the pond is taken just below the surface of the pond, the effluent temperature is assumed to be representative of the pond as a whole. In March the pond temperature was less than 10^{o}C. This temperature is usually the lowest at which nitrification can be effectively maintained, and at 10^{o} C the growth rate of nitrifying organisms is approximately a 16-day doubling time. Based on the rule of thumb that 1 pound of NH_3-N will result in 0.17 pounds of bacterial growth, you would need:

(16 days-lbs/lbs) x (0.17 lbs bacteria/lbs NH_3-N) = 2.72 lbs bacteria/lbs NH_3-N/day **Equation 2-15**

To nitrify 600 lbs/day of NH_3-N at this temperature you would need 1,440 lbs of active nitrifying bacteria in the pond. Since the temperature is even colder than this in the winter, and the ammonia concentration is low during the winter, it would take some time for this amount of bacteria to develop. As the temperature warms to 20°C in June, the growth rate increases to some 4 days doubling time, reducing bacterial mass requirement to 380 lbs to nitrify 600 lbs/day of NH_3-N. By July, the temperature is 25^{o}C, providing time for additional bacterial growth and further reducing the need for bacterial mass for nitrification, and the rate increases again.

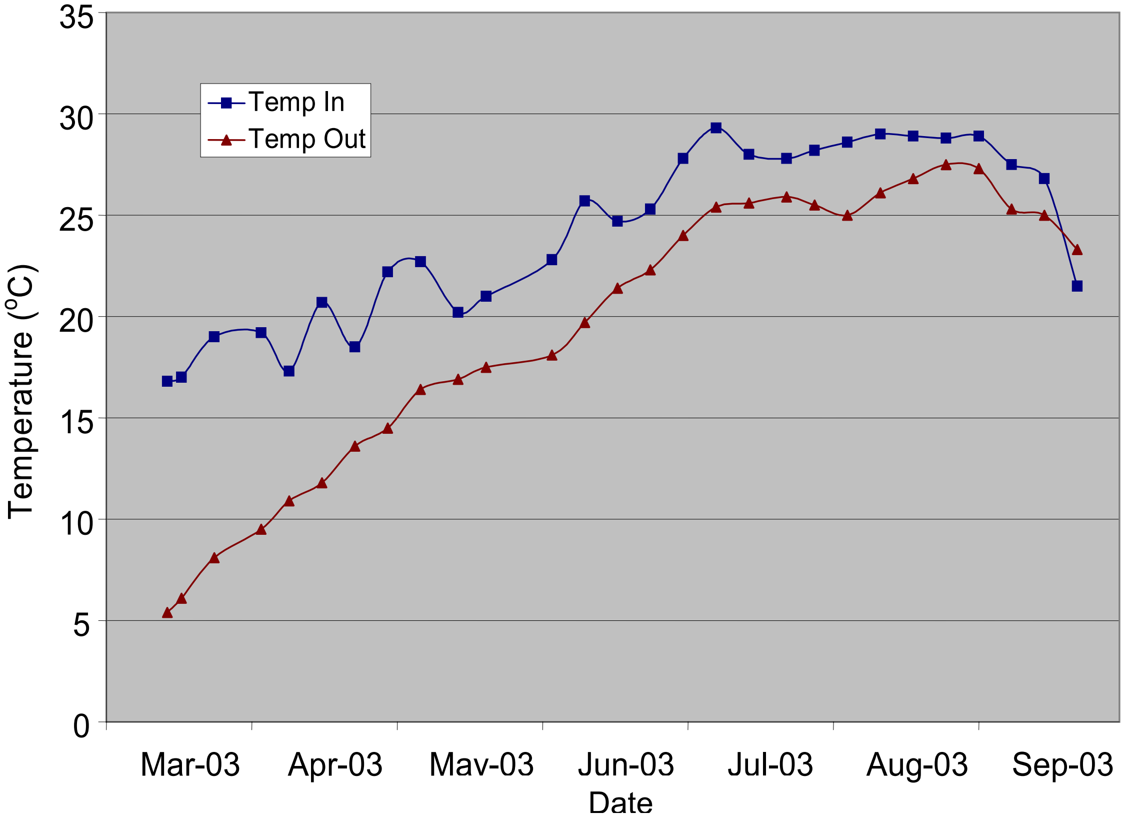

Figure 2-9
Inlet and Outlet Pond Temperatures 2003

Figure 2-10 shows the temperature data for 2003 through 2005. Year 2003 was warmer than 2004, which could offer some clue as to the reduced nitrogen loss this second year. However, 2005 was warmer than 2003, yet showed a similar nitrification behavior as 2004. Figure 2-11 shows a plot of ammonia removal rate as a function of pond temperature. For this plot, the 2003 data for April and May are deleted, since the nitrogen removal during these months did not result in formation of nitrite and nitrate and therefore are probably related to algal assimilation. It can be seen from this plot that significant nitrification does not occur until the pond temperature reaches or exceeds 20°C.

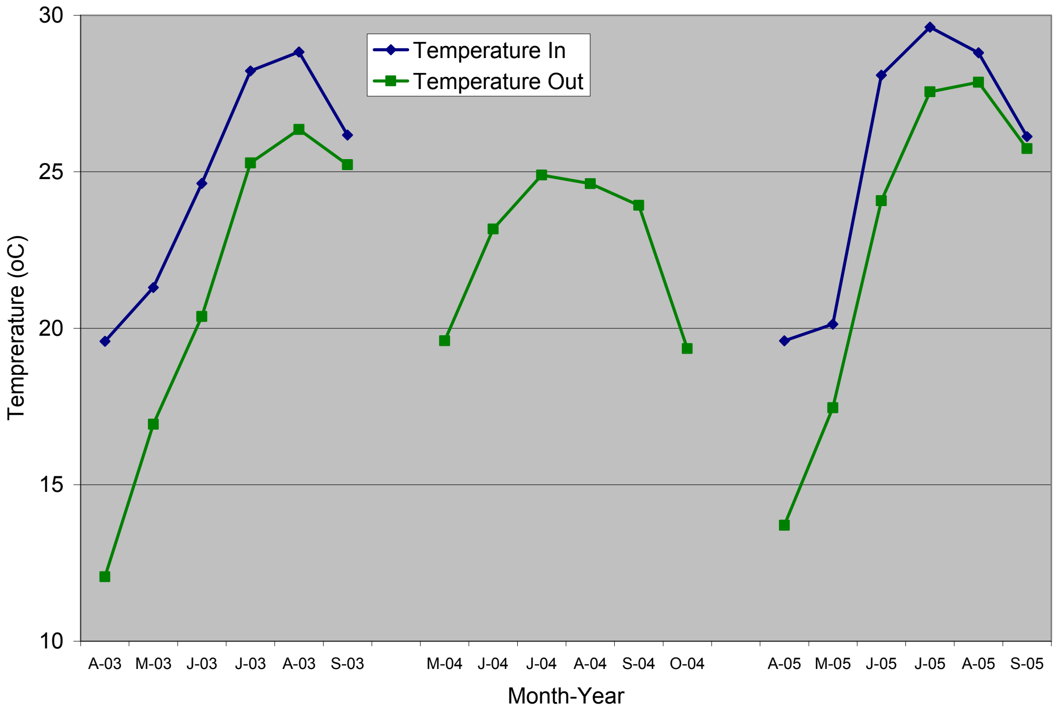

Figure 2-10
Inlet and Outlet Temperatures 2003 through 2005

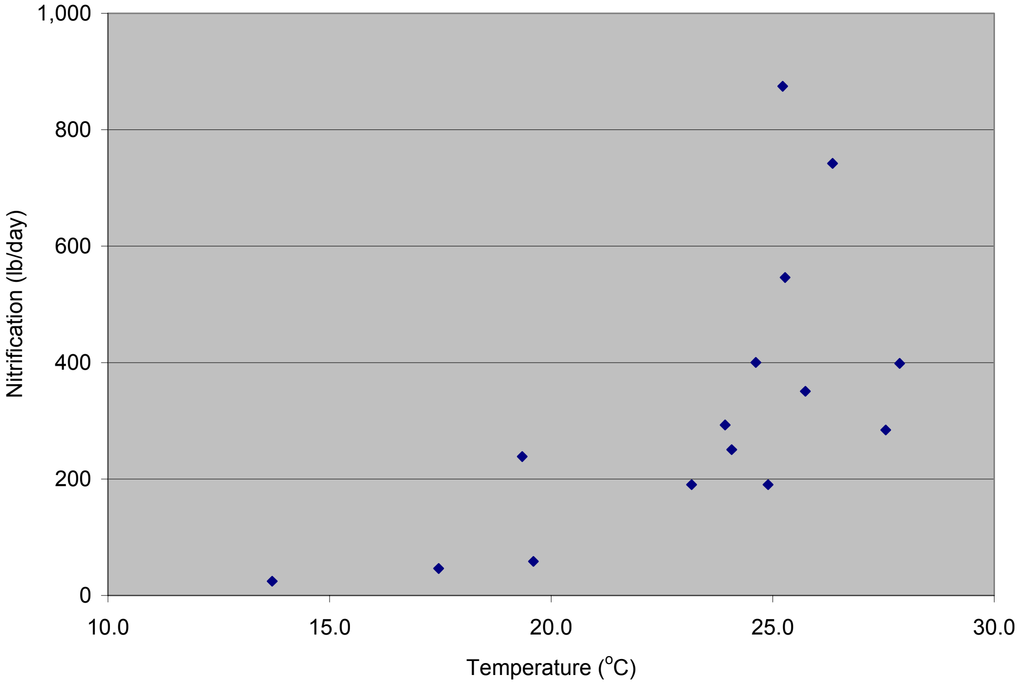

Figure 2-11
Effect of Temperature on Rate of Ammonia Loss

Nitrification is also very sensitive to pH and alkalinity. At a pH of less than 6.5, nitrification is inhibited. The influent and effluent pH of the pond are shown in Figure 2-12. Caustic addition is shown in Figure 2-13. Figure 2-14 shows the influent alkalinity after caustic addition and the effluent alkalinity. In 2003, the influent water was frequently below 6.5. In May, the operator of the pond reported starting to add about 2,300 lbs/day of sodium hydroxide, equivalent to 2,900 lbs/day of alkalinity, which is sufficient for about 400 lbs of NH_3-N nitrification. As nitrification increased in July through September (Figure 2-8), the pH in the pond dropped despite the caustic addition. By September, caustic addition was increased to 3,300 lbs/day of sodium hydroxide, which reversed the pH slide and resulted in the highest removal rate of NH_3-N for the year. This was despite the pH of the pond being less than the desired minimum of 6.5.

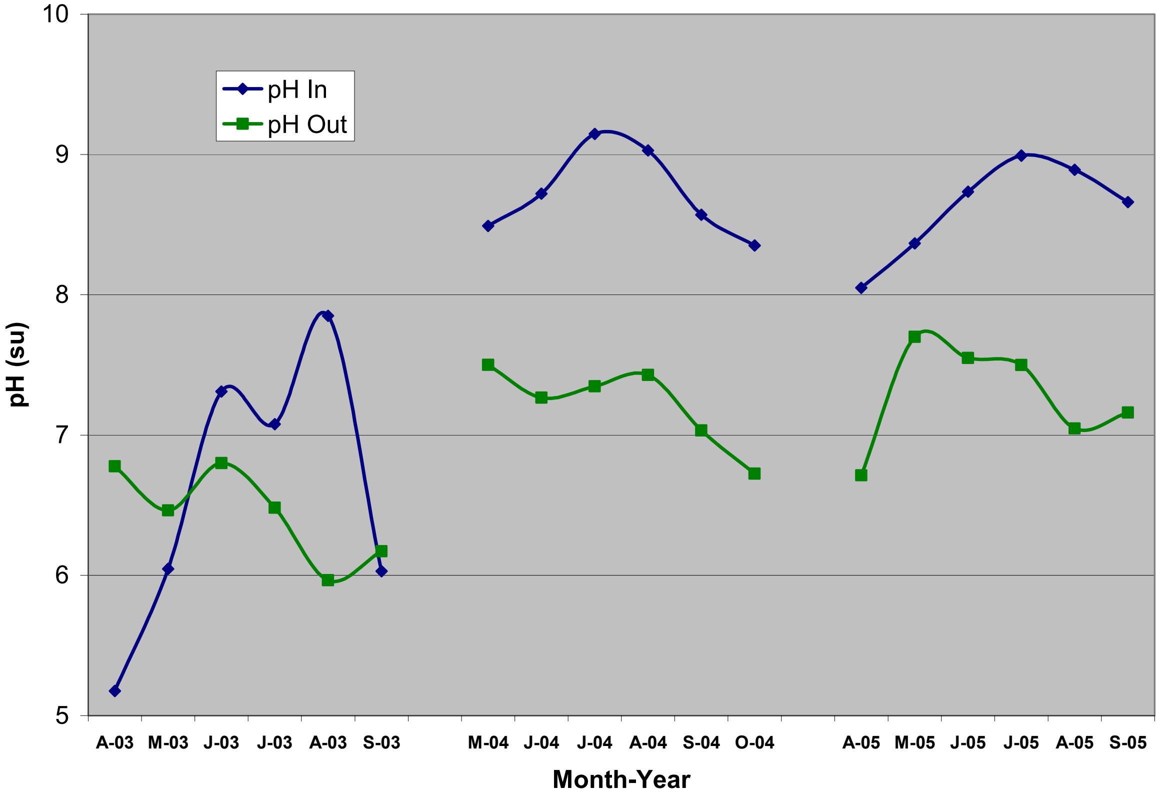

Figure 2-12
Influent and Effluent pH, 2003 through 2005

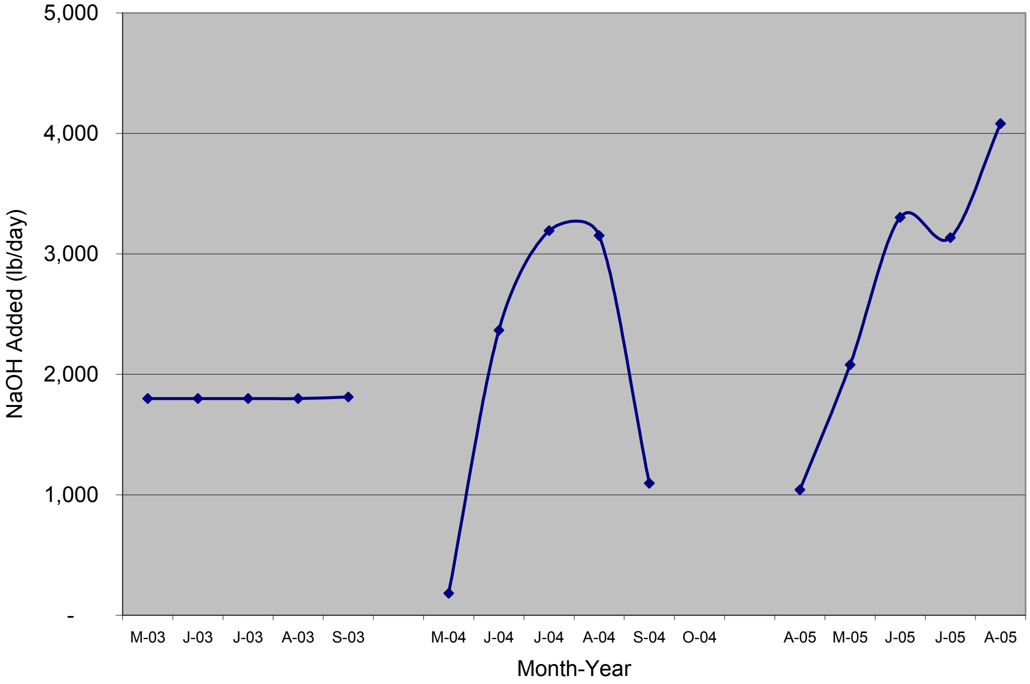

Figure 2-13
Caustic Addition, 2003 through 2005

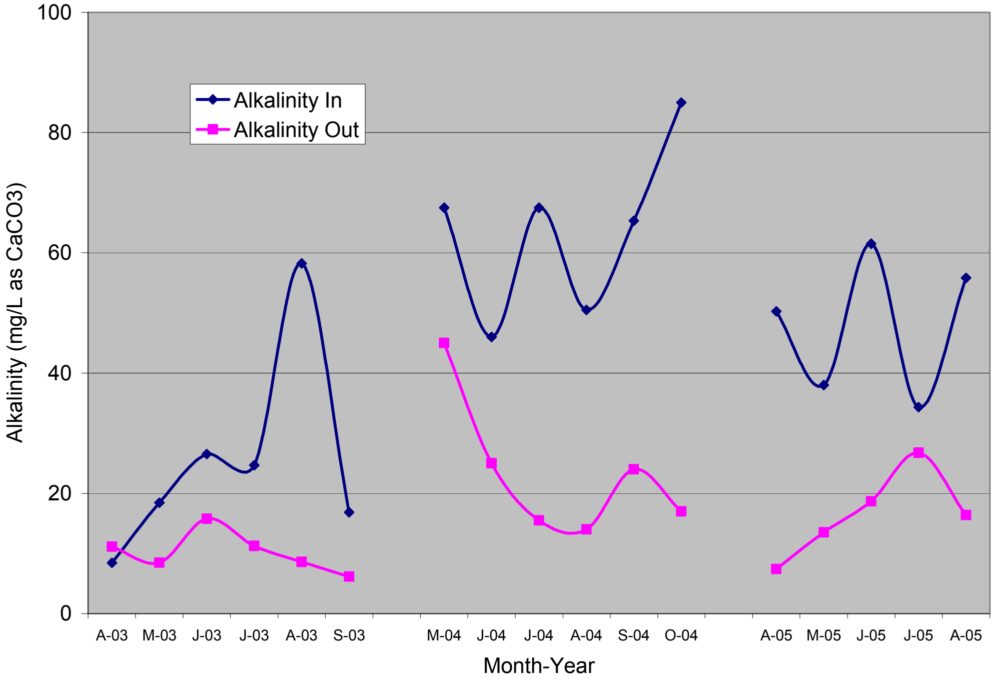

Figure 2-14
Influent and Effluent Alkalinity, 2003 through 2005

In 2004 and 2005, caustic addition was increased resulting in the pond pH staying above 6.5 throughout each of these summers. However, this improved pH was accompanied by reduced rates of nitrification. It is not clear why the 2004 and 2005 performance differed from 2003; it is known that it is not due to pH, alkalinity, or temperature, which were similar.

One potential explanation is that 2003 was the first year that plant staff manipulated the pond to promote algae and bacteria growth by feeding large quantities of phosphorus and alkalinity (as caustic). The 2003 spring and fall ammonia loss can be attributed to algae assimilation. If these algae had stayed in suspension, TSS limits would have been exceeded (which did not happen), so it is assumed that they settled. Settled algae could have been anaerobically decayed, releasing ammonia to the water in 2004 and 2005, in addition to the power plant discharge of fly ash. This ammonia release may explain difference in apparent ammonia consumption seen in 2004 and 2005 versus 2003. Actual assimilation of ammonia may have been the same, with half assimilated by algae and half nitrified. Release of ammonia from the decay of the previous year's algae reduced the amount that could be contributed by the the plant without exceeding the capacity of the pond. The ammonia mass balance only includes the mass of ammonia in the influent and effluent, but does not include the ammonia released in the pond due to decay.

Figure 2-15 shows the consumption of alkalinity based on a daily mass balance analysis of the difference between the influent effluent alkalinity plus the change in alkalinity in the pond. Figure 2-16 shows the alkalinity consumption as a function of ammonia destruction. In 2003, the ratio of alkalinity consumption to ammonia loss is close to the nitrification consumption of 7.14 lbs of alkalinity per lbs of NH_3-N converted. The higher ratio of 2004 and 2005 indicate that the poorer nitrification is not due to pH or lack of alkalinity.

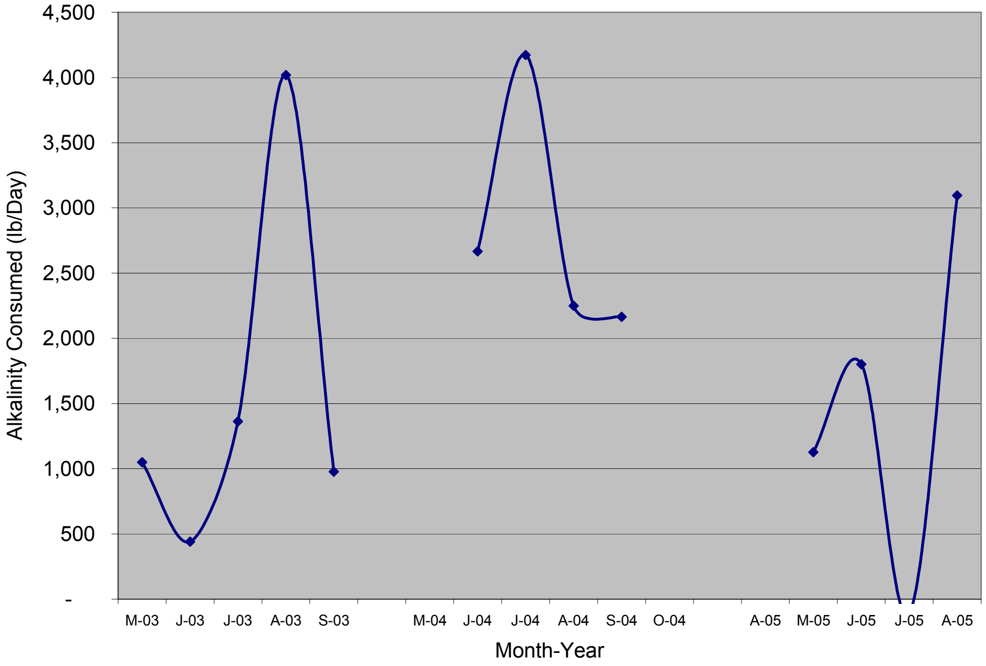

Figure 2-15
Alkalinity Consumption, 2003 through 2005

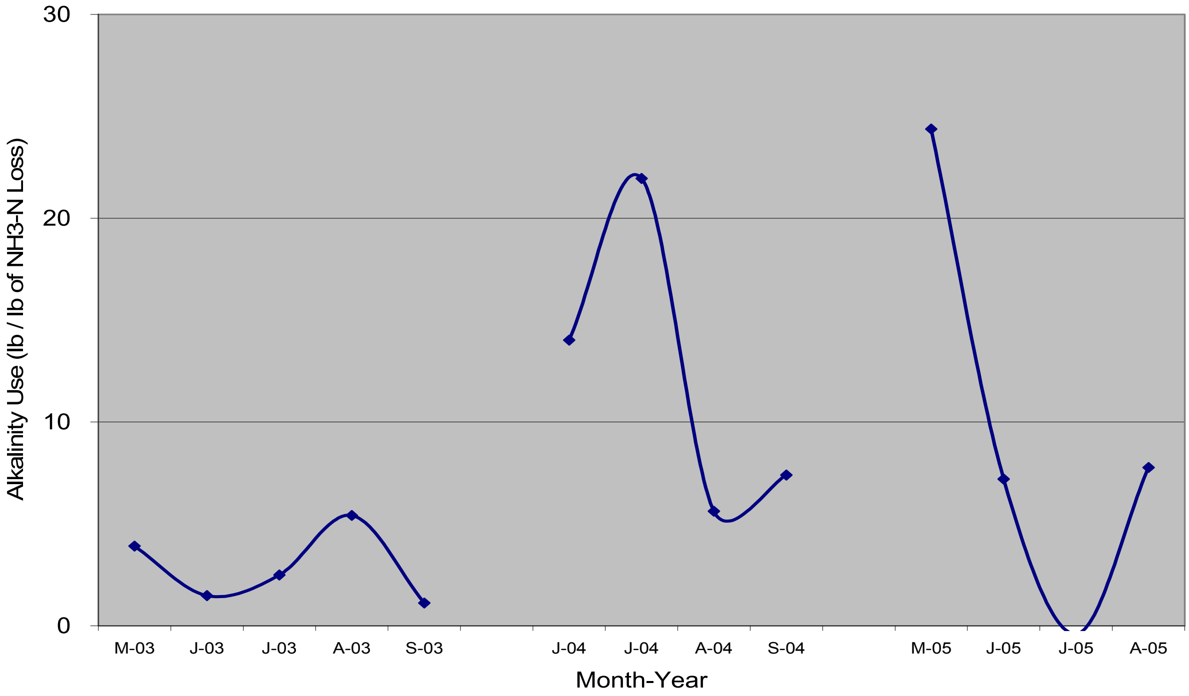

Figure 2-16
Alkalinity Consumption as a Function of Ammonia Reduction, 2003 through 2005

Conclusions

1. A mass balance of ammonia and nitrite and nitrate species is a good method of determining extent of nitrification in an ash pond subject to ammonia discharge.. Using a mass balance can help gain an understanding of treatment mechanisms at work and allow for optimization of these mechanisms.
2. The major portion of ammonia removal in the subject ash pond appears to be by nitrification.
3. Nitrification is slow to start in the spring until the pond temperature rises to 20°C.
4. The first summer there appeared to be significant algal assimilation in the early spring.
5. In subsequent years this additional removal by algal assimilation did not seem to be significant, possibly due to equilibrium with algal decay and release of ammonia from previous year.
6. The pH of the pond was maintained within a range that was conducive to nitrification by the addition of sodium hydroxide.

Case Study #2 – Managing NH_4^+ and TSS in a Midwestern Sluiced Ash Handling System

The studied system consists of primary and secondary fly ash cells in series, with a tertiary polishing pond which discharges to a river. Bottom ash is sluiced to a bottom ash cell (which is regularly dredged for sale as road grit, etc.). Effluent from the bottom ash cell flows through a coarsely channelized vegetated area and then into the same polishing pond as the fly ash side. In all of the cells, nutrients (N & P) were monitored along with total suspended solids (TSS), total volatile suspended solids (TVSS, reported as percent volatile of the TSS), and several other parameters beyond the scope of this discussion (e.g., chlorophyll, pH, dissolved oxygen, alkalinity, etc.).

The drivers for conducting this project were:

- The need to reduce TSS, which was experiencing occasional excursions above discharge limits (e.g., Figure 2-17), and
- The need to develop plans for managing algal biomass that is sure to greatly increase once ammonium loads to ash pond systems increase as a result of installation of SCRs.

Although it had been used in the past, copper sulfate was not a desirable alternative for large scale elimination of phytoplankton biomass. A management approach based on ecological principals was sought. The initial step was to determine the limiting nutrient(s), if any, and then attempt to reduce its concentration, i.e. loading rate to pond, which would have the effect of reducing algal biomass. At the same time, it was desirable to manage the pond so that blue-green algae did not become dominant. Blue-green algae can be toxic and unpalatable to zooplankton. Blue-green algae dominated systems can become “dysfunctional”. Energy stops flowing up the food chain. Higher trophic levels become starved, and N and P are then released back to the water as dead algae decomposes.

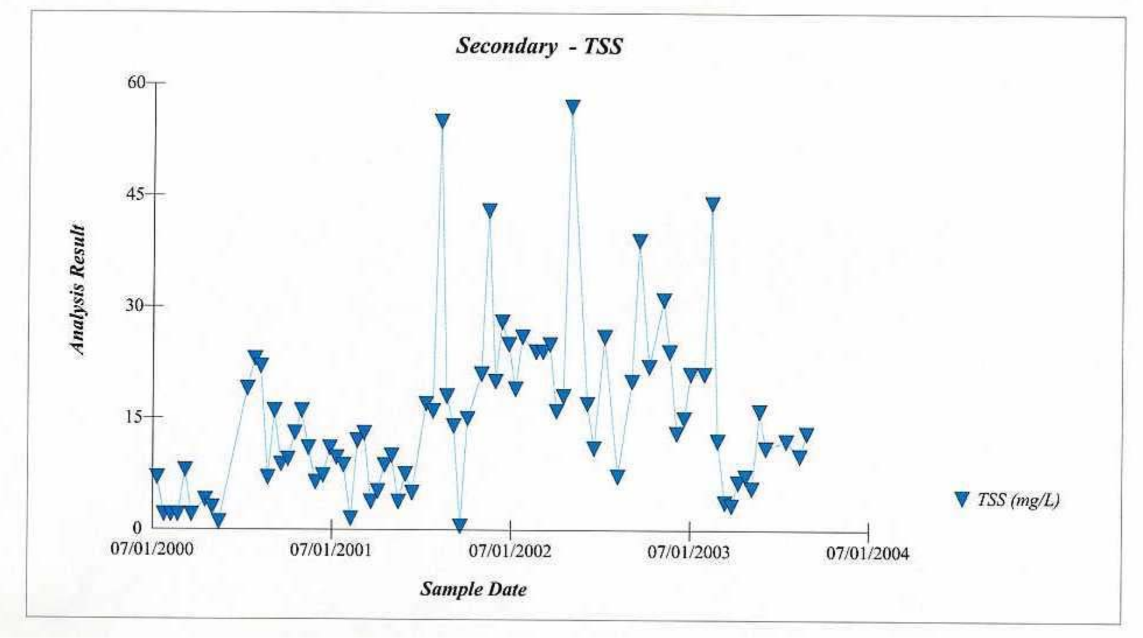

Figure 2-17
Occasional Excursions in the Secondary Fly Ash Pond of TSS (mg L^{-1}) Above Permit Limits were Resulting from Algal Blooms, Rather than from Suspended Ash

The drivers identified above address related problems. There was an immediate need to reduce algal biomass that was causing the excursions of TSS, yet it was realized that the future will bring increased ammonium loading to ponds as a result of SCRs, and this will be accompanied by even greater algal productivity and biomass. This latter point is supported by the fact that all of the ponds in this system demonstrated chronic nitrogen limitation of algal production, i.e. the N:P ratio was generally well below the 16:1 ratio (e.g., Figure 2-18)**,** indicating that any added nitrogen (e.g., ammonium or nitrate) would stimulate an algal bloom, sending TSS even higher. (See Chapter 2 for more on N:P ratios). Because the entire pond system demonstrated nitrogen limitation most of the time, it was concluded that future increases in ammonium loadings from ammonia slip from SCRs will generate even greater amounts of algal biomass and TSS. It may be possible to seek relief for the volatile fraction since the TSS limits in current permits are designed to regulate the amount of fly ash discharged to the receiving water.

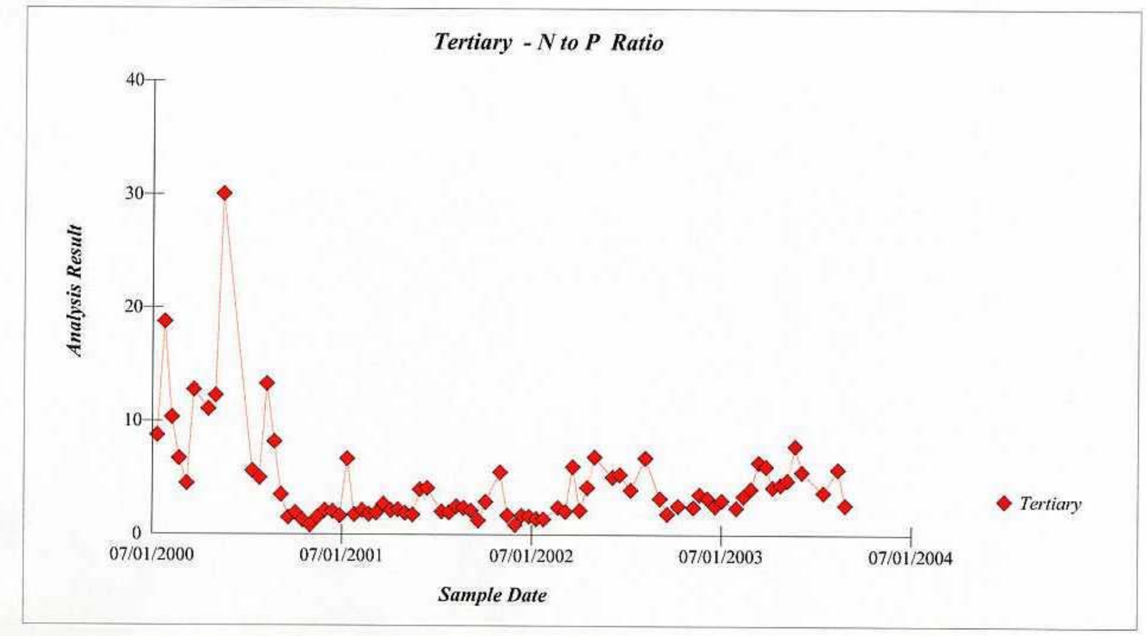

Figure 2-18
N:P Ratio in the Polishing Pond. Points Above the Value of 16 Indicate Potential for Phosphorus Limitation. At those Times any Additional Phosphorus Loading to the Pond can Stimulate an Algal Bloom. When Values are Below 16, any Additional Nitrogen Loading can Stimulate Algal Growth

The sources of nutrients to the ash pond system consisted of fly ash, bottom ash, plant runoff, and plant sewage. In the future, FGD sludge will be evaluated.

TSS in the polishing pond (Tertiary) exhibited several excursions (Figure 2-19). However, during excursions above 30 mg L^{-1}, the TSS was generally > 50% volatile, indicating the presence of algal biomass (Figure 2-20). The lowest values of TVSS coincide with the lowest TSS values at times when algal biomass was low.

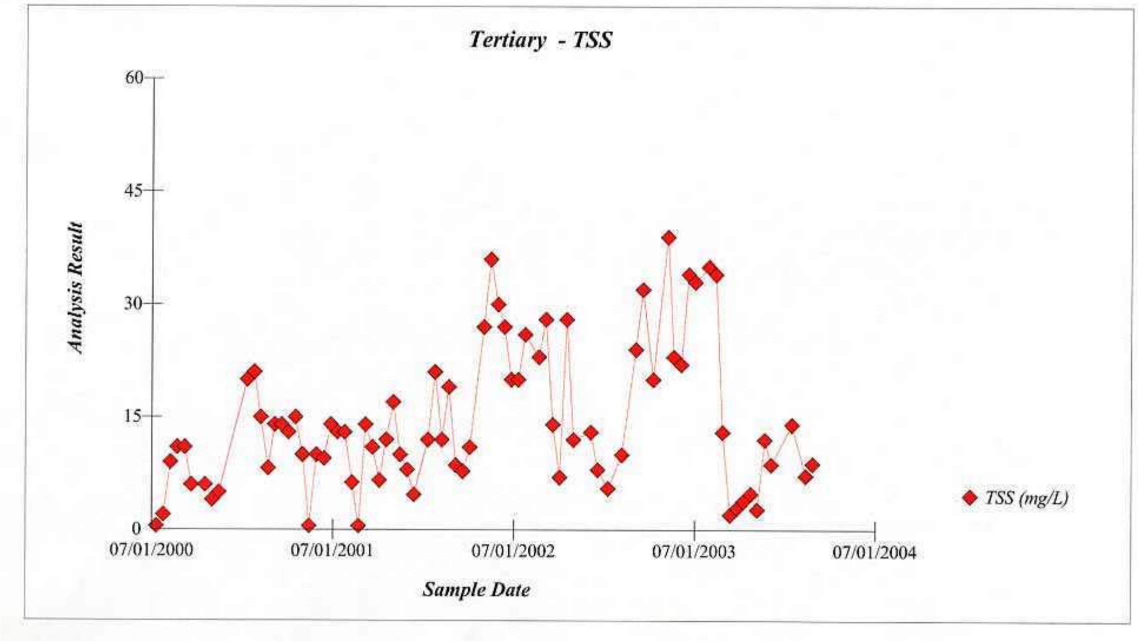

Figure 2-19
TSS (mg L^{-1}) in the Tertiary Pond had Even More Excursions than the Secondary Pond

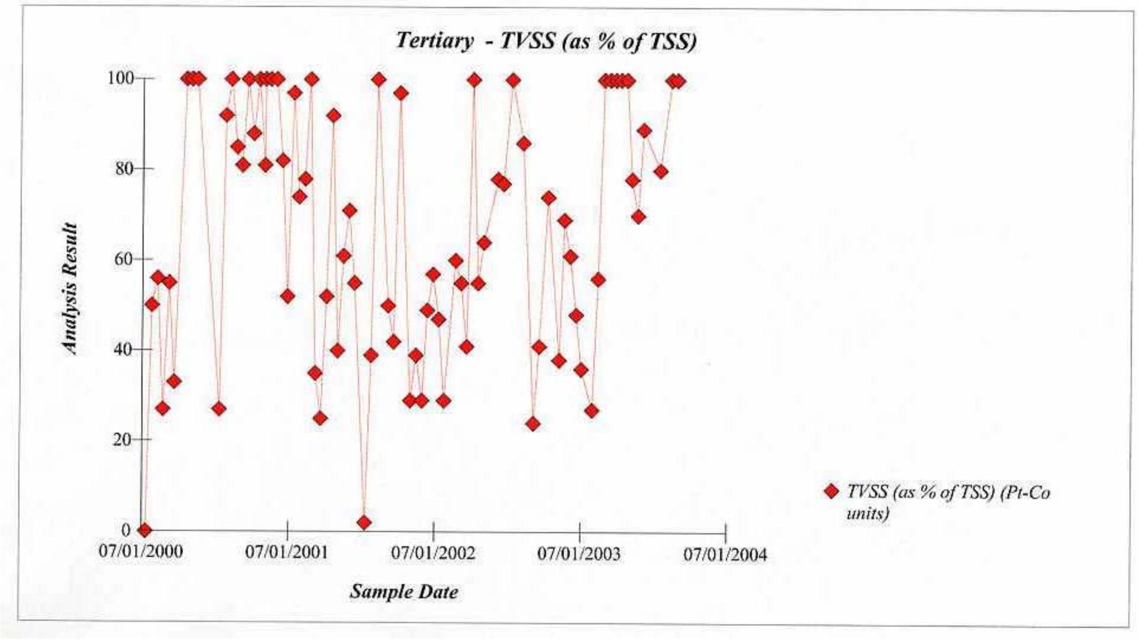

Figure 2-20
TVSS (as % of TSS) in the Tertiary Pond

Preliminary Conclusions of the Study

- Increased ammonium loading leads to increased algal biomass and large diel swings in pH due to photosynthesis during day time, because ash ponds are often poorly buffered.
- An integrated management approach is necessary to deal with interrelated parameters (TSS, TVSS, pH, etc.).
- Bottom ash and fly ash can have different N:P ratios. It may be advantageous to manage them as separate discharges (i.e. not mix them in the polishing pond), in order to avoid stimulating algal growth and elevated TSS in the polishing pond.
- Regulators should be urged to provide relief for the volatile fraction of TSS.
- Ponds should be evaluated for their assimilative capacity for ammonium once future loading rates are determined (from SCR, etc.).

Ash Pond Design To Improve Ammonia Removal

When new ash ponds are needed at new facilities or to replace ponds whose storage capacity has been exhausted, the design of the new ponds should incorporate features that will enhance ammonia removal. These features are described in the following sections.

Pond Hydraulic Configuration

The hydraulic configuration of the ash pond can have a significant impact on treatment efficiency of the pond, due to short-circuiting (or the lack thereof due to good design). The location of the inlet and outlet can affect the hydraulic efficiency of the pond. When the inlet is positioned directly opposite the location of the outlet, short-circuiting of the flow directly across the pond surface is likely, causing a reduction in treatment efficiency. To minimize this, various pond configurations can be used to improve the flow path through the pond, resulting in less short-circuiting and an increase in the actual HRT. The ideal flow path is a long and narrow flow path (i.e., plug flow type of configuration). A short and wide flow path, such as a square or circular pond, is undesirable. Since ash pond location and configuration are constrained by the sites that the plant has available, internal floating baffles or fixed berms can be added to more closely approach the ideal condition. Examples of potential methods to improve the flow path in non-ideal ponds are shown in Figure 2-21.

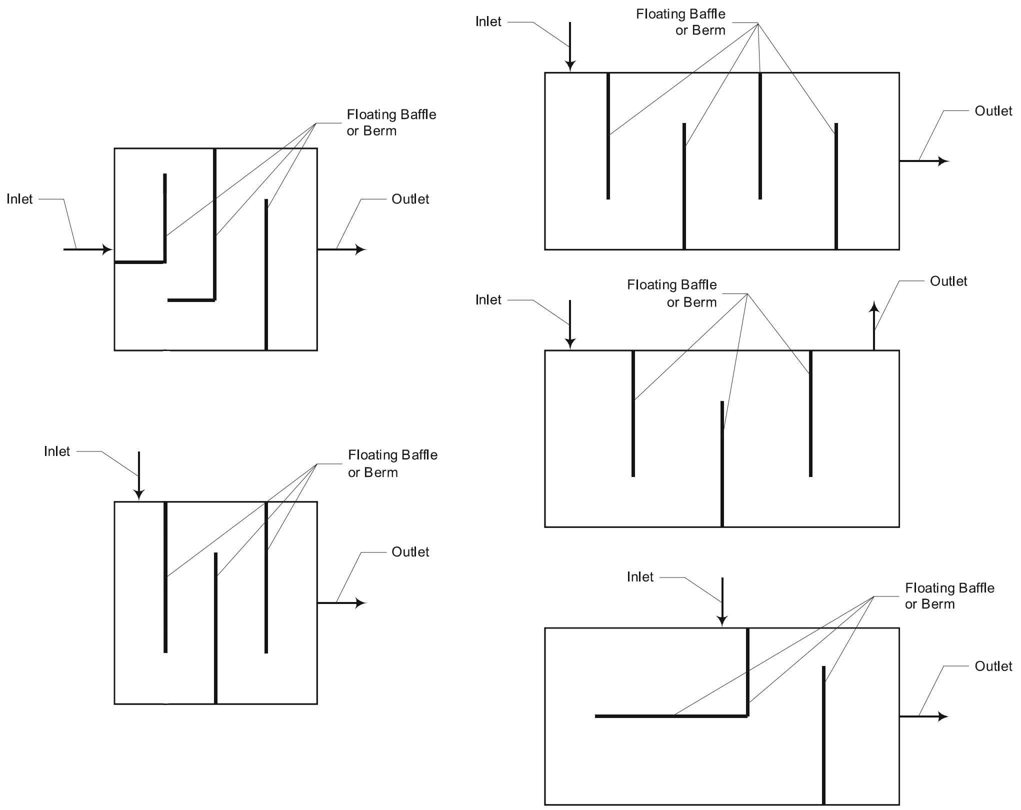

Figure 2-21
Methods to Improve the Flow Path in Non-Ideal Ponds

Pond Size and Depth

Where nitrification and algal assimilation are being used for ammonia removal, the total surface area and the depth of the pond can affect the treatment efficiency. In general, a pond with a large surface area and shallow depth is preferred to a deep pond with a small surface area.

Nitrifiers in ash ponds will be a combination of free-floating and fixed-film (i.e., attached to rocks, plants, and debris on the bottom and sides of the pond). A large surface area will result in a greater area of fixed-film nitrifiers and increase the ammonia removal capability, versus just free-floating nitrifiers. The large surface area will also provide a large photic zone for the growth of algae, increasing algal assimilation.

Shallow ponds (i.e., <25 feet deep) provide several benefits over deep ponds (>25 feet deep) in removal of ammonia. The benefits include:

1. Shallow ponds are less likely to thermally stratify, which can reduce the actual HRT of the pond.
2. Shallow ponds are less likely to be subjected to anoxic conditions on the bottom, since they will be more completely mixed.

3. When mechanical means of aeration are utilized, the added DO is more likely to disperse throughout the pond depth. In deep ponds, the circulation of the aerator may not be able to penetrate deep enough into the pond, thus leaving the potential for anoxic conditions to occur.

Treatment Wetlands

Surface-flow treatment wetlands offer an option for ammonia removal that will generally require a lower degree of active management as compared to promoting nitrification within the ash pond. Treatment wetlands have been used successfully by municipalities and industry for over 20 years for removal of a variety of pollutants.

Treatment wetlands function as land-intensive biological treatment systems. Inflow water containing particulate and dissolved constituents spreads through a large area of shallow water and emergent vegetation. Physical, chemical and biological processes operate within the wetlands which lead to the removal of the constituents from the wastewater, including ammonia.

A treatment wetland system can be incorporated at the end of an existing or new ash pond to provide ammonia removal. Such a treatment wetland would consist of three separate cells to approximate a plug-flow reactor. Each cell is one-third of the total wetland area. The flow from one cell to another is controlled to maintain approximately one foot of surface water in the wetland. Following the last cell, a small clearwater pond is provided for settling of particulate material from the wetland and reaeration prior to discharge. Figure 2-22 shows a schematic of an ash pond incorporating a treatment wetland.

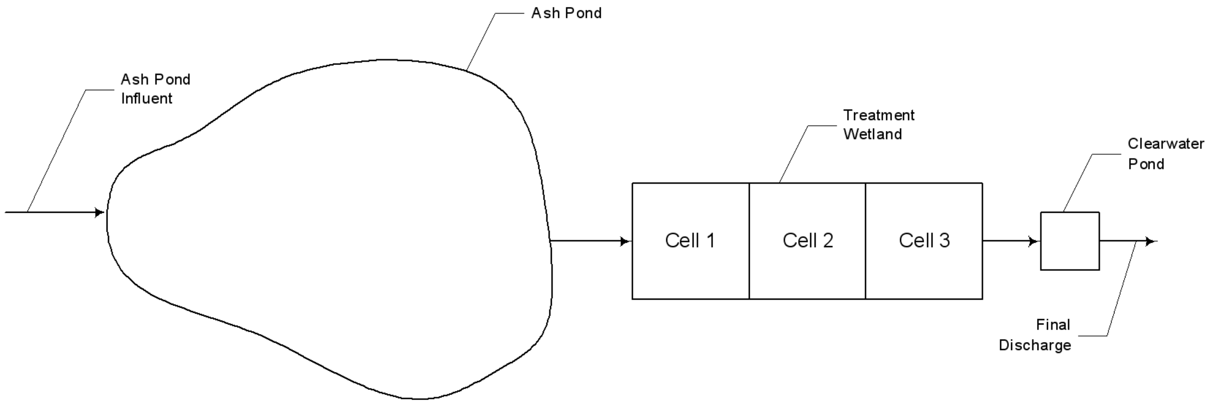

Figure 2-22
Schematic of Ash Pond and Treatment Wetland

The transformation and removal of the pollutants entering the wetland can be modeled by using a first-order, area-based, plug-flow model, as developed by Kadlec and Knight [8]. In its simplest form, the model is described by the following equation.

$$A = \frac{Q}{k_{20} \times \Theta^{T-20}} \times \ln\left(\frac{C_e - C^*}{C_i - C^*}\right)$$ **Equation 2-16**

Where:

$A = area\ of\ wetland, m^2$

$Q = flow\ rate, m^3 / day$

$k_{20} = removal\ rate\ at\ 20°C, m / yr$

$\Theta = temperature\ correction\ factor, dimensionless$

$C_e = effluent\ concentration, mg/L$

$C_i = influent\ concentration, mg/L$

$C^* = background\ concentration, mg/L$

For ammonia, *k* is 18 m/yr, Θ is 1.04, and C^* is 0.0 mg/L of NH_3-N. Assuming a treatment wetland having an influent flow rate of 5 mgd, an influent ammonia concentration of 10.0 mg L^{-1} of NH_3-N, an effluent ammonia limit of 5.0 mg L^{-1} of NH_3-N, and a minimum temperature of 15°C, the area required is approximately 80 acres.

3

TSS

Sources of TSS in Ash Ponds

Primary sources for TSS in ash ponds include fly ash handling, FGD purge streams, bottom ash handling, algae growth in the pond, and sediments naturally occurring in the plant's source water. The following sections will describe each of these sources. It is important to note that the extent to which the TSS from each of these sources eventually contributes to effluent TSS varies. This will be discussed after the discussion of sources.

Fly Ash Handling

Fly ash is the very small particulate residue resulting from the combustion of the coal. The fly ash exits the boiler in the flue gas. The flue gas will pass through the economizer and air preheater before entering the air pollution control system, where the fly ash it is removed from the flue gas.

ESPs are commonly used to remove the fly ash and other fine particles from flue gas. The particles are removed intermittently by rapping the collector plates, causing the collected particles to fall by gravity to a hopper in the bottom of the ESP. The fly ash is removed from the hopper by either a dry ash handling system or by wet-sluicing the ash to the ash pond.

The TSS concentration of wet-sluiced fly ash can range from about 1,000 mg L^{-1} to over 100,000 mg L^{-1}, depending on the type of boiler and coal being used. Studies by EPRI at sites with tangentially-fired boilers using pulverized eastern bituminous coal indicated an average of around 20,000 to 30,000 mg L^{-1} [6, 9]. Another EPRI study site with front-fired boilers using pulverized eastern bituminous coal averaged between 50,000 to 70,000 mg L^{-1} [7].

A fraction of the fly ash will consist of spherical, hollow particles called cenospheres. Cenospheres have a specific gravity (S.G.) between 0.6 and 2.0. Fly ash can contain up to 80% cenospheres, depending on the type of boiler used, the type of coal used, and operating conditions. Typically, cenospheres with an S.G. less than 1.0 constitute much less than 1% of the fly ash produced, and cenospheres with an S.G. less than 2.0 but greater than 1.0 constitute around 10% of the fly ash. Cenospheres with an S.G. near 1.0 will tend to remain suspended in the pond, those with a greater S.G. will settle to the bottom of the pond, and those with a lower S.G. will float to the pond surface. Even though the percentage of cenospheres with an S.G. less than 1.0 is much less than 1%, they still could lead to TSS issues. Assuming a fly ash concentration of 30,000 mg L^{-1} and 0.01% of cenospheres with an S.G. less than 1.0, the resulting TSS would approximately 3 mg L^{-1} of TSS. If there were 0.1% cenospheres and fine ash particles with an S.G. less than 1.0, then that would equate to approximately 30 mg L^{-1}. Cenospheres are wind- and current-driven, and often build up in one or more portions of the pond. When that area is near the effluent, the impact on effluent TSS will be higher.

Even if wet-sluicing of the fly ash is not used, fly ash may still be discharged to ash ponds from maintenance and washdown of the following:

- Economizer
- Air heater
- Dry ash handling equipment
- Surrounding areas (for dust control)

The quantities of fly ash from the sources are small in comparison to that collected in the ESP. Typically, these sources will represent less than 5 to 10% of the total fly ash. However, fine particles and cenospheres produced during these washes can still periodically cause TSS concerns in the pond.

Wet FGD Purge Stream

Wet FGD scrubbing systems are used to control SO_2 emissions from plants after the flue gas has passed through the ESP. Fly ash that was not removed in the ESP is entrained in the FGD scrubber water. A fraction of the FGD scrubber water is purged from the system to avoid corrosive levels of ions and the buildup of fine solids. The purge water is high in TSS, which includes the entrained fly ash as well as other solids (e.g., calcium sulfite [$CaSO_3$], calcium sulfate dihydrate [$CaSO_4 \bullet 2H_2O$, or gypsum]) generated in the FGD process that are not settled out and removed in the FGD liquid-solids separators (i.e., hydroclones).

Typically, the FGD purge stream is discharged to a treatment system to separate the solids from the liquid. However, if the purge is not treated separately but is discharged directly to the ash pond, then it can contribute a large concentration of TSS to the pond. Like fly ash sluice water, FGD purge stream water can contain difficult-to-settle fine particles and therefore has potential to impact effluent TSS levels. The solids introduced from FGD systems are primarily gypsum, which may actually dissolve when diluted into an ash pond, decreasing settling efficiency.

Bottom Ash Handling

Bottom ash is coarse ash particles, formed in boilers using pulverized coal, and is too heavy to be carried out in the flue gas. The bottom ash falls to the bottom of the boiler, where it is collected in a hopper. The bottom ash is removed from the hopper by either a dry ash handling system or by wet-sluicing the ash to the ash pond.

The TSS concentration of wet-sluiced bottom ash can range from about 500 mg L^{-1} to over 4,000 mg L^{-1}. However, these solids are easily settled out in a pond. In these studies, the sluice waters were allowed to settle. After settling, and the supernatant contained 4 to 200 mg L^{-1}, with a median of 40 mg L^{-1} [6, 7, 9].

Algae Growth

Algae growth in the ash pond will also contribute to the TSS in the pond. The degree to which algae growth will affect the TSS concentration is dependent on the nutrient (nitrogen and phosphorus) loading to the pond. As the nutrient loading to a pond increases, the algae population in the pond will generally increase. The nutrients can come from several sources including:

- Atmospheric deposition
- Runoff
- Decomposition of plants and animals
- Sources internal to the facility

Generally, nutrients from **atmospheric deposition** and **decomposition of plants and animals** will be low and not change the natural background level of algae in a pond. Nutrients from runoff can be significant if the runoff water comes from an agricultural area, due to the application of fertilizer. Internal sources, such as ash conditioning, SO_3 mitigation, and SCR or SNCR, can also increase the nutrient loading, primarily due to the addition of ammonia.

Internal sources will generally be of most concern when considering algae growth in ash ponds. Algae will use the nutrients to grow and produce new cells. For every 1 mg L^{-1} of ammonia nitrogen (NH_3-N) assimilated by algae, approximately 16 mg L^{-1} of new algae will be produced, which translates to a 16 mg L^{-1} increase in the TSS concentration. (See Section 4 for further details.)

Fate of TSS in Ash Ponds

Ash ponds are predominantly designed based on disposal volume. Pond design also has factored in TSS removal as facilities face TSS limits. The quantity, physical characteristics, and ultimate disposition of the ash will control the size of the ponds.

Bottom Ash Ponds

Bottom ash is generally sand sized with grain size ranging from fine sand to fine gravel (less than 0.075 millimeters (mm) to 3/8 inch or greater). The S.G. is on the order of 2.5. Assuming a grain size of 1.0 mm, the settling rate is approximately 6 feet per minute (fpm). Based on this rate, the bottom ash will settle almost immediately when discharged to the pond.

Bottom ash ponds are typically small due to the high settling rate. Bottom ash can easily be removed from the pond by dredging, and freely drains, allowing annual removal of the ash. The recovered ash can be used by the facility or sold to outside companies for a variety of applications. These applications include:

- Snow and ice control
- Aggregate in lightweight concrete masonry units

- Raw feed material for portland cement
- Aggregate in cold mix emulsified asphalt mixes, base or subbase courses, or in shoulder construction
- Structural embankments
- Backfill/drainage media

Fly Ash Ponds

Fly ash particle sizes generally range from 1 to over 100 micrometers (µm). The specific gravity (S.G.) is on the order of 2.5. Assuming a grain size of 10 µm, the settling rate is approximately 1.0 foot per day. This shows that the settling rate of fly ash is much lower than that of bottom ash, but still fast enough that the majority of the fly ash will settle close to the inlet of the pond.

When new (or newly dredged), fly ash ponds typically provide an overflow rate (a commonly used criterion for clarification design) that is much better for settling then typical designed settling treatment devices such as clarifiers. Over time, however, settled fly ash will form an "ash delta" at the inlet of the pond, and when this happens ponds can become much smaller, which can result in carryover of TSS into effluent. Typically, plants will raise the level of an ash pond once this begins to occur to improve settling. In a pilot study of fly ash ponds, TSS a short distance outside of the ash delta soon was less than 45 mg L^{-1}, despite the fact that the ash sluice water entering the pond had an average TSS concentration of 2,800 mg L^{-1} [10]. This was equivalent to 98% removal of the influent TSS. By the mid-point of the pond, the TSS was less than 30 mg L^{-1}, or 99% removal. Figure 3-1 shows the TSS concentration versus the distance from the pond inlet. Similar results have been seen at other facilities [6, 7, 9].

The presence of significant quantity of fly ash particles and cenospheres with an S.G. less than 1.0 will pose a TSS issue in the pond. These particles will float to the pond surface and will be readily discharged in the effluent. Furthermore, cenospheres can block light penetration and inhibit algal photosynthesis.

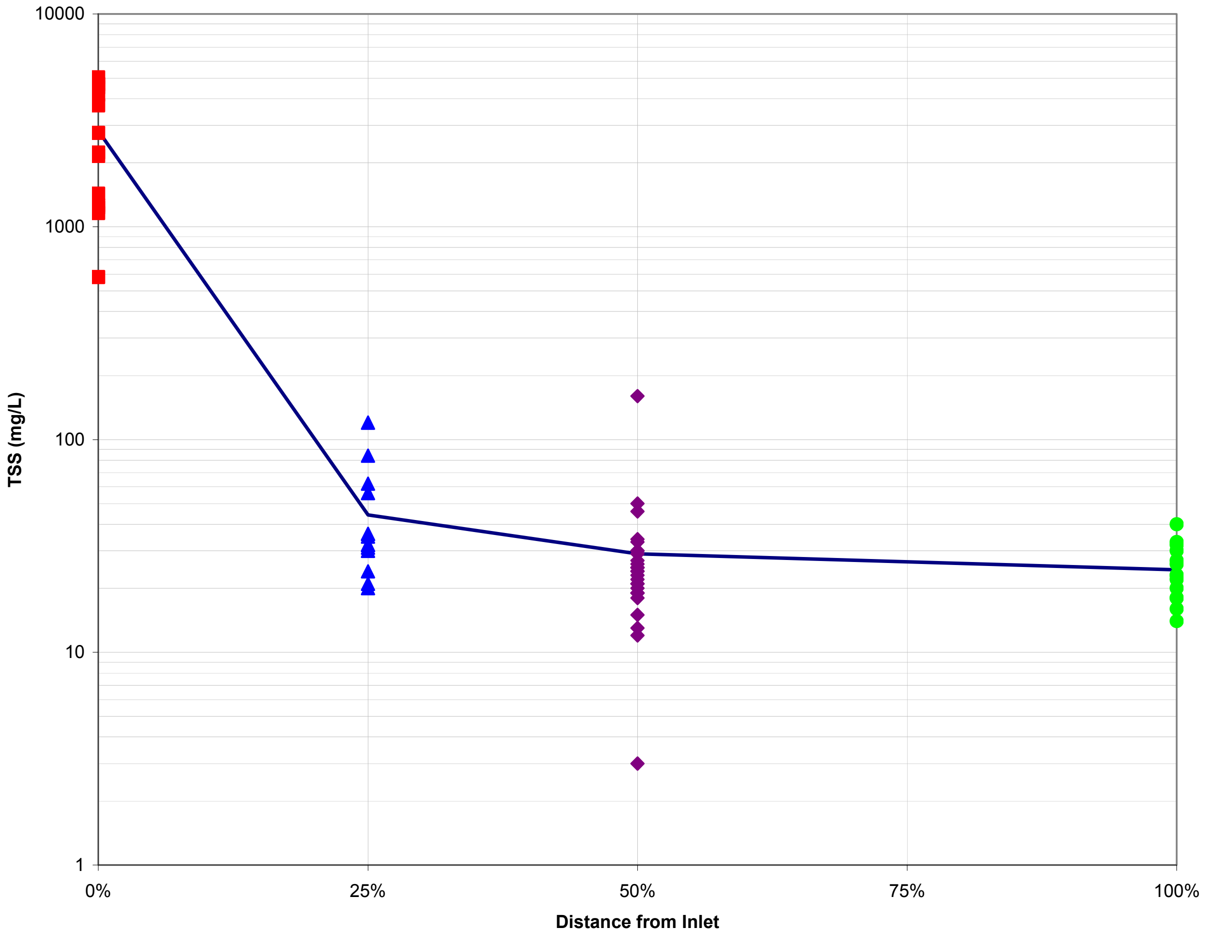

Figure 3-1
TSS Concentration Versus Distance from Inlet

TSS Management Options

As discussed above, ash ponds will generally remove greater than 99% of the TSS entering the pond. Average discharge TSS concentrations from fly ash pond from four EPRI studies were between 5 to 24 mg L^{-1}, with a maximum of 40 mg L^{-1}. However, under some circumstances, the removal of TSS may not be sufficient to meet the categorical standard limits of 30 mg L^{-1} monthly average and 100 mg L^{-1} daily maximum. These include:

- Poor hydraulic conditions
- Low density particles
- Surface runoff
- Excessive algae growth

Poor hydraulic conditions in the pond can include short-circuiting, insufficient surface area, and excessive velocity at the outlet. Short-circuiting, either caused by the wind or unsuitable location of the inlet relative to the outlet, can result in currents in the upper layer of the ponds that carry the TSS at a rate greater than the settling rate. If this happens, the TSS will not have sufficient time to settle before being carried over in the effluent. Methods to reduce short-circuiting, discussed in Section 2, can be implemented to improve the time available for settling the TSS.

In order for a particle to settle completely to the bottom of a pond, the horizontal velocity of the water in the pond must be less than or equal to the settling rate of the particle to be settled. Figure 3-2 shows this graphically.

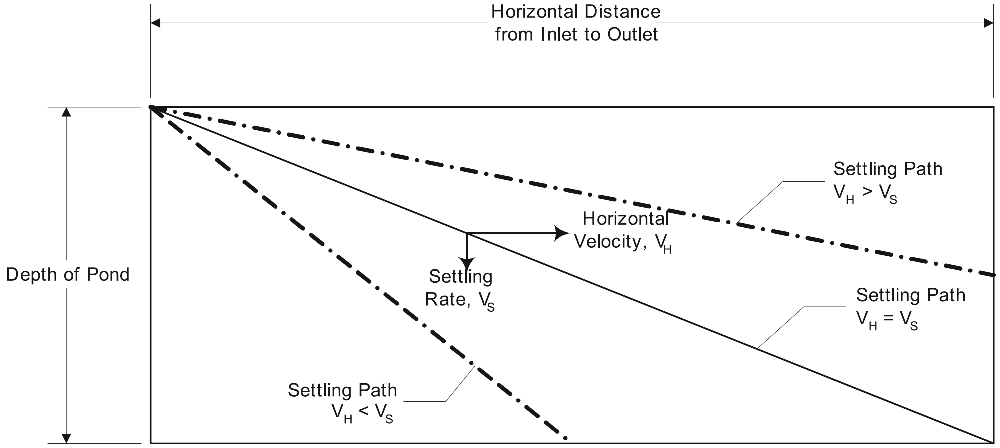

Figure 3-2
TSS Concentration Versus Distance from Inlet

As the ash delta grows further into the pond, the horizontal distance from the inlet to the outlet will decrease, with a resulting reduction in the surface area. If the horizontal distance decreases to a point such that the particle is unable to settle to the bottom of the pond, then the particle will remain suspended in the effluent.

High velocities near the effluent weir or pipe, caused by constricting the area through which the water must pass, may cause the settled particles to be re-suspended and carried out in the effluent. To prevent this, the location, number, and size of the outlet(s) must be considered in the planning and design of the pond.

If nitrification is being used for ammonia removal within the pond, the location of the surface aerators must take into consideration the formation of the ash delta and the effluent location, so as not to re-suspend the particles near the pond discharge. Surface aerators create a circulation pattern in the pond. The depth and diameter of that pattern depends on the horsepower of the mixer. When placed too close to the influent, the circulation induced by the aerators will affect the settling of the ash. When placed too close to the effluent, the circulation may re-suspend particles that have already settled.

When particles with an S.G. equal to or less than 1.0 are present, such as some cenospheres, algae, and bacteria, they may need to be removed to prevent violating the TSS discharge limits. Potential methods to remove these particles include physical removal by skimming them off the surface or the addition of polymer to coagulate the particles.

Physical removal can be accomplished by:

- Using booms placed across the width of the pond to funnel them to a collection point
- Installing a baffle around the effluent weir or pipe which directs them to a collection box

From the collection point or box, the particle can be pumped or vacuumed out. If the particles are primarily cenospheres, they could potentially be sold for use in construction and other products.

Polymer addition can be used where the effluent TSS consists of particles with poor settling characteristics, such as colloidal solids, and some bacteria and algae. The polymer will act as a coagulant. When the polymer comes into contact with particles it will be adsorbed on the particle. The particle and polymer will come into contact with other particles (with or without polymer adsorbed to them). As this happens, the diameter of the total particle will increase, resulting in an increase in the settling rate of the particle.

Stormwater run-off from the area around the pond can contribute to the TSS concentration. Ponds are typically surrounded by dirt or gravel access roads to provide access to the influent channel/pipe and the outlet weir/pipe for routine monitoring and maintenance. During rain events, the dust and dirt on the access road will wash into the pond. The amount of TSS washed into the pond will depend on the intensity and duration of the event. The outlet area will be most susceptible to problems from this increase in TSS, since there may not be enough distance to allow the particles to settle. To minimize the occurrence of this problem, sediment and erosion controls, such as a silt fences or diversion channel, could be implemented to reduce the amount of solids reaching the pond or to divert the run-off away from the pond.

Algal growth can lead to increased TSS in the pond, and may result in increases in effluent TSS concentrations. **Pond turnover** due to thermal stratification can also result in short-term TSS increases.

4
PH

Operations Impacting pH in Ash Ponds

Multiple waste streams affect the pH of ash pond water. The acidity or alkalinity of the different waste streams varies widely based on the source of the stream. This section will discuss the large-volume waste streams that will affect the pH of the ash pond.

Fly Ash Sluicing

Studies conducted at multiple power plants as part of the Power Plant Integrated Systems-Chemical Emissions Study (PISCES) have shown that the pH of fly ash sluice water is a function of the composition of the coal being used [11]. The sluice water pH is related to the calcium, sulfate, and iron content of the fly ash produced during combustion of the coal. Fly ash with a high calcium content results in a higher pH sluicewater, while fly ash with a high sulfate content results in a lower pH. During combustion, calcium is oxidized to CaO (quicklime) and sulfur is oxidized to SO_2 and SO_3. When mixed with water in the sluicing process, CaO forms $Ca(OH)_2$ which raises the pH. The SO_2 and SO_3 react with water to produce sulfurous and sulfuric acid, respectively, lowering the pH. CaO and SO_3 react to produce $CaSO_4$ (gypsum), which has no impact on pH.

A predictive relationship for fly ash sluice water pH was developed from the PISCES studies. The relationship is based on the difference between the number of moles of calcium and the number of moles of sulfate in the fly ash [11]. If the difference is less than 0.01, then the pH is predicted by Equation 4-1. When the difference is greater than or equal to 0.01, then the pH is predicted by Equation 4-2.

$$\text{pH} = 0.8 * \exp^{(300 *(\text{Moles of Ca - Moles of Sulfate in ash}))} + 3.8$$ **Equation 4-1**

$$\text{pH} = 0.6 * \log(\text{Moles of Ca - Moles of Sulfate in ash} - 0.0039) + 12$$ **Equation 4-2**

The pH predictive relationship was able to predict the pH of sluice water within 1.5 pH units for 20 of the 27 samples for which a full ash characterization was available [11]. Figure 4-1 shows the predicted pH versus the actual pH for these samples.

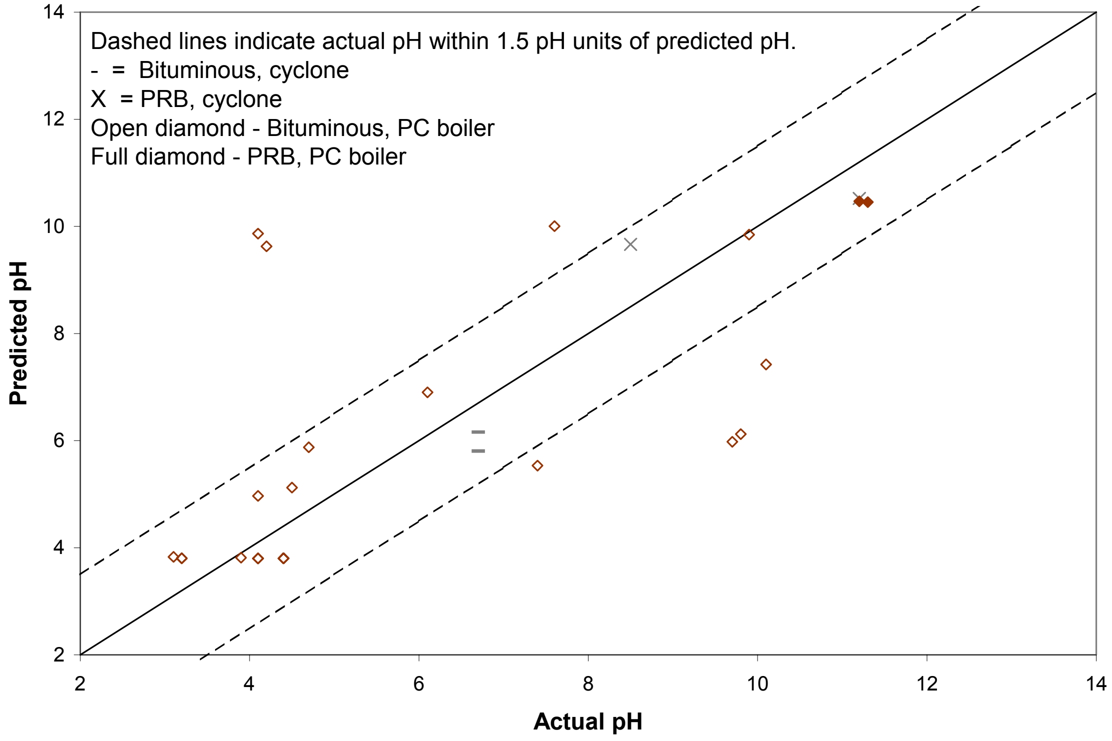

Figure 4-1
Predictive Relationship from Fly Ash to Sluice Water pH

Bottom Ash Sluicing

Bottom ash sluice water tends to have a pH more neutral than fly ash sluice water. Average values from the PISCES studies ranged from 5.6 to 6.4. Fly ash ranged from 3 to 12 [6, 7].

Coal Pile Runoff

Coal pile runoff can be very acidic. The pH of coal pile runoff in the PISCES database from bituminous coal piles ranges from 1.5 to 3.1. Coal pile runoff pH is related to the coal type, as shown in Table 4-1.

Table 4-1
Relationship of Coal Type to Runoff pH

Coal Type	Percent Sulfur	Recorded pH	Number of Samples*
Bituminous	1.8% - 4.1%	2.1 to 3.1	41
	0.9% - 1.5%	2.8 to 4.4	
Sub-bituminous	Not available	7.4 to 9.3	3

* Uses data from PISCES sites and historic data.

Pyrites Pile Runoff

Runoff from pyrites (FeS_2) piles resulting from coal processing activities can also produce a very acidic waste stream. The aqueous oxidation of pyrites proceeds through a series of complex reactions, with the final products being ferric iron and sulfuric acid. The overall reaction is represented by the Equation 4-3.

$$FeS_2 + 11\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 19\ H^+$$ **Equation 4-3**

As shown in Equation 4-3, 14 moles of H^+ are produced for each mole of FeS_2 oxidized, which will produce a runoff from the pyrite pile with a very low pH.

Demineralizer Regeneration

Demineralizer regeneration wastes will be alternately acidic and caustic. Regeneration of anion beds is usually accomplished with sodium hydroxide, which raises the pH. Regeneration of cationic beds is done with sulfuric acid, which lowers the pH. Mixed beds are separated for regeneration, requiring both acid and caustic for regeneration. The regeneration process alternates acid and caustic addition, resulting in a waste stream that is first acidic, then caustic, as shown in Figure 4-2. Despite dilution by other waste streams, the demineralizer regeneration may cause significant brief swings in the pH of ash pond influent. However, the swing in the pH tends to be dampened in the ash pond.

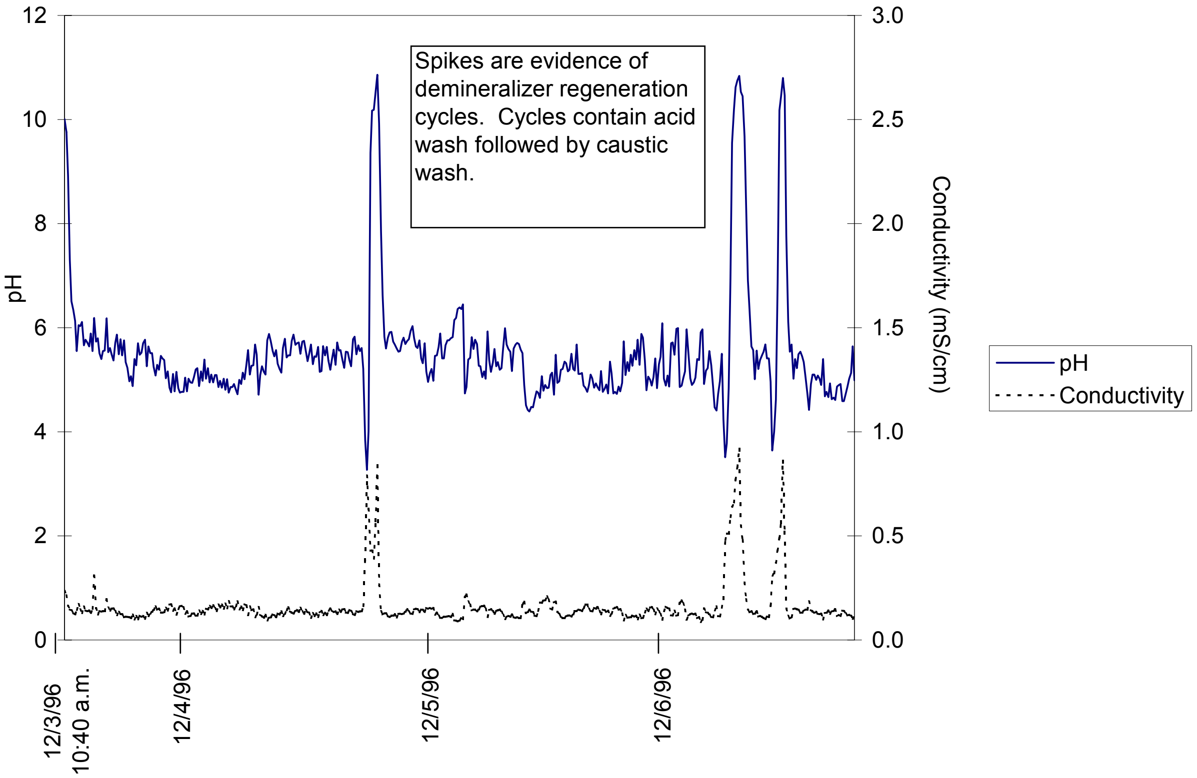

Figure 4-2
Effect of Demineralizer Regeneration on Ash Pond Influent

Where significant concentrations of carbonate are present in the raw water, the cation resin is followed by a de-aeration in which carbonates are stripped as CO_2. This reduces the load on the anion bed relative to the cation bed, and can result in an imbalance between acid and caustic usage for regeneration, making the combined regenerant acidic.

Mitigation of SO_3

When ammonia is added to the gas phase to control SO_3, the ammonia and SO_3 react to produce ammonium bisulfate, a salt particle that is removed subsequently by a baghouse or ESP along with the fly ash. When the ash is sluiced with water, the ammonium bisulfate dissociates to ammonia and sulfuric acid, lowering the pH of the sluice water.

Ash Conditioning

Ash conditioning, using various chemical treatments, has been used to improve the efficiency of ESP. Two of the primary chemicals used to condition the ash are ammonia and SO_3. As discussed above and in Section 1, when ammonia is used, it will react with SO_3 in the flue gas to create ammonium bisulfate. When the ash is sluiced, the ammonium bisulfate dissociates to ammonia and sulfuric acid, lowering the pH of the sluice water.

If SO_3 is used for ash conditioning, the SO_3 is adsorbed by the fly ash to increase the resistivity of the ash, which improves the efficiency of the ESP. When this ash is sluiced, the water and SO_3 will react to produce H_2SO_4, which will decrease the pH of the sluice water.

Equipment Cleaning Waste

Equipment such as the air preheater, ESP, and boiler are cleaned using various chemical cleaners and high-pressure water. This produces a low volume waste stream that can have a pH lower than other waste streams (if fly ash is acidic) or higher (if fly ash is alkaline). During the initial phase of cleaning, the pH will be at its lowest and will increase as the cleaning progresses. The equipment cleaning generally occurs when most generating equipment is off-line and, as such, is not diluted by other waste streams before entering the ash pond.

The cleaning waste stream pH from air preheaters can vary widely depending on the coal being used. Observed initial pH values have ranged from 3.0 for units using high-sulfur coal to 5.6 for units using low-sulfur coal [9]. The pH from ESP cleaning waste streams have ranged from 3.1 to 4.0 [9]. The acidic pH cleaning waste stream could affect pH of ash ponds if the volume of water is significant. Figure 4-3 shows the impact of a boiler wash on the ash pond influent [10].

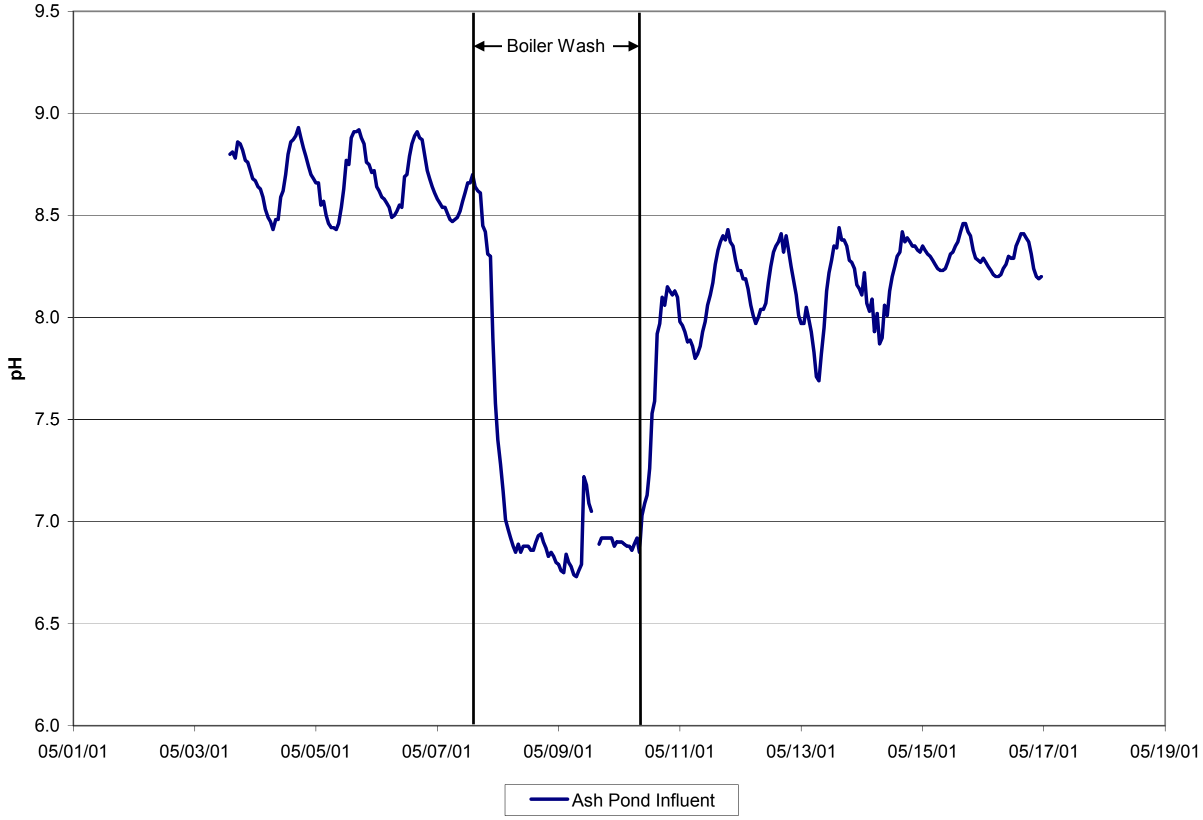

Figure 4-3
Effect of Boiler Wash on Ash Pond Influent

Fate of pH in Ash Ponds

In general, the pH of ash pond water tends to move toward a neutral pH (7.0), whether the ash pond influent pH was acidic or alkaline. Figure 4-4 shows an example of the in pH from the influent and effluent of a pond [10].

If pyrites are piled in a partially submerged pile they can generate acidic runoff, similar to coal pile runoff. If pyrites are sluiced to a pond and settle out to become completely submerged, it tends to be a neutral stream.

As discussed in Section 1, the growth of algae will impact the pH of ash ponds. Algae removes CO_2 from the water during daylight (photosynthesis) and release CO_2 back to the water during nighttime (respiration). The change in CO_2 throughout the day will change the carbonate equilibrium within the pond. Consumption of CO_2 causes an increase of the pH of the water. Conversely, release of CO_2 will tend to decrease the pH of the water. This cycle will create a diurnal pattern in the pond pH. If high nutrient loads, either from ammonia in the pond influent or surface runoff from agricultural activities, are applied to the pond, an increase in the algae population can occur. If the growth becomes excessive, the amplitude of the diurnal pH cycle can be significant enough to fall outside of the categorical pH discharge limits of 6.0 to 9.0.

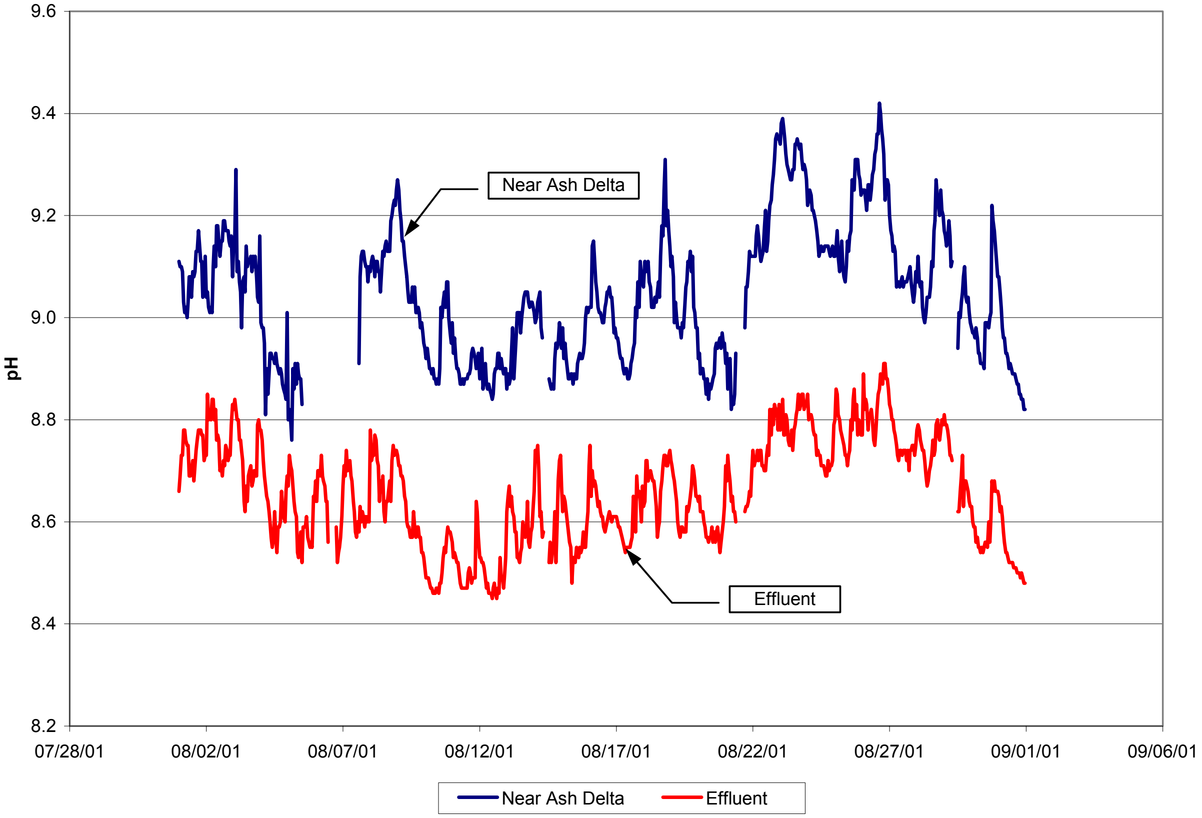

Figure 4-4
pH Change from Near the Ash Delta to the Pond Effluent

On the other hand, ammonia removal by biological nitrification results in acidification of the pond water. As discussed in Section 1, nitrification consumes 7.14 mg L^{-1} of alkalinity (as $CaCO_3$) for each 1.0 mg L^{-1} of NH_3-N removed. If the alkalinity of the water is low, the pH of the pond water will decrease. The optimum pH range for nitrifiers is between 7.5 and 8.6. If the pH drops below 7 or far above 9, the nitrification will be significantly inhibited. At a pH of 6.5 or 9.5, the nitrification rate will be half of the maximum rate [12]. Therefore, control of pond pH is critical when nitrification is used for ammonia removal.

pH Management Options

The primary option for in-pond management of pH is chemical addition to adjust the pH upwards or downwards to meet the discharge limits for pH. Addition of caustic soda (sodium hydroxide, NaOH) is typically used to increase the pH of the water. Lime may also be used to increase pH. Addition of either CO_2 or an acid, such as sulfuric acid, is typically used to decrease the pH of the water.

When raising the pH with NaOH, the NaOH will combine with atmospheric CO_2 to produce bicarbonate alkalinity if there is adequate air transfer to the water. The reaction is described by Equation 4-4.

$NaOH + CO_2 \rightarrow Na^+ + HCO_3^-$ **Equation 4-4**

The bicarbonate will neutralize acid, producing CO_2 and water, as shown in the reversible Equation 4-5.

$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$ **Equation 4-5**

Bicarbonate is desirable as it also tends to keep the pH near neutral. When raising the pH, the bicarbonate reacts with the hydroxide (OH^-) to produce carbonate ions and water, as shown in Equation 4-6.

$OH^- + HCO_3^- \rightarrow CO_3^{-2} + H_2O$ **Equation 4-6**

Carbonates are needed by algae or bacteria for ammonia assimilation or for nitrification. The algae need the carbon as a building block for growth. The bacteria require large amounts of alkalinity, due to the acidic reactions involved with nitrification.

When lowering the pH with CO_2, the increase in CO_2 will increase the production of bicarbonate and H+, as shown in Equation 4-5, to maintain the equilibrium. The increase in H^+ will lower the pH of the water.

When lowering the pH with acid, the acid will dissociate in the water into H^+ and its conjugate base. For example, sulfuric acid (H_2SO_4) will dissociate into 2 H^+ and SO_4^{2-}. The increase in H^+ will decrease the pH of the water.

The point of application of chemicals to adjust the pH of the pond water can potentially have an impact on more than just the pH. Simulation studies have shown that adding caustic during sluicing of fly ash would limit the dissolution of toxic metals from the fly ash [7].

To prevent large swings in pH resulting from equipment cleaning wastes, the cleaning wastes could be equalized or thoroughly mixed with other wastewater to reduce spikes in pH.

Minimizing the use of SO_3 and/or ammonia for fly ash conditioning limits the production of ammonium bisulfate and will help control the production of H_2SO_4, which would otherwise acidify the sluice water. Similar benefits apply to minimizing the use of ammonia for the mitigation of SO_3 and in SCR and SNCR systems.

Selection of the type of coal being used can help control the pH of sluice water. As discussed earlier, the calcium content of the coal has a direct relationship to the pH of the fly ash sluice water. A coal with a high calcium content will generally have a higher pH than coals with a low calcium content.

5

RECOMMENDED FUTURE RESEARCH

Adjustment of pH and removal of suspended solids are well understood, and so no research is recommended to improve our understanding of these factors.

On the other hand, ammonia use is significantly increasing due to the expanded use of ammonia fly ash conditioning, NOx reduction, and SO_3 mitigation, at the same time that there is increased regulation of ammonia and total nitrogen discharge. The relatively new high concentrations of ammonia being discharged to ponds is beginning to overcome their natural assimilation capacities.

There are technologies that compete with ammonia, but these technologies, such as Trona injection for SO_3 mitigation, are much more expensive than ammonia utilization. There are also well-developed tank-based treatment processes that can treat ammonia. However, these are much more expensive to operate than ash ponds. So it is worthwhile to develop ways to manipulate ash ponds to increase their natural ability to assimilate ammonia.

As a result there is a need to better understand the mechanisms and pathways for ammonia assimilation in ash ponds, and to test methods to manipulate the ponds to improve their performance.

Aeration and Mixing

After algae assimilate ammonia, they can die and settle to the bottom of the ash pond. The resulting organic material can produce anoxic conditions in the bottom layer of the pond, resulting in re-release of the ammonia. The anoxic condition on the bottom prevents nitrifying bacteria from surviving or nitrifying the ammonia. Stratification of the pond in the winter traps this ammonia until it is released during the spring overturn, which is also the time when ammonia is first fed for SCR operation, and is the time when there is a low population of nitrifying bacteria. Further testing is needed on the effectiveness of the use of mixer/aerators to eliminate stratification, maintain aerobic conditions on the bottom year-round, eliminate spring release of ammonia, and promote bacterial growth in the spring.

Use of Nitrifier Incubators

The spring increase in use of ammonia occurs at a time when there is a low inventory of nitrifiers. Sluice water tends to be warm, but cools rapidly when it is mixed with a large cold body of water such as an ash pond. This ammonia is also diluted by mixing with the large volume of an ash pond. Bacterial growth is limited by this initial low ammonia concentration and cold temperature. If the pond were segregated into an initial small pond (e.g., 1-day HDT) and a larger pond, this initial pond would have a higher ammonia concentration and a higher temperature than the rest of the pond system, and would serve as an incubator, growing a nitrifying population that would spill over into the rest of the pond system, speeding up the rate at which the pond system can acclimate to the ammonia feed. Such an incubator could be constructed out of a floating curtain across the first section of pond.

Some plants use cooling tower blowdown as a water source for sluicing fly ash. For plants that do this, it would be useful to investigate if, instead of taking the sluice water from the cold side of the cooling tower, that this be switched to using the hot side water for ash sluicing in the spring. Increasing the pond temperature earlier in the spring would assist in growing bacteria earlier to handle the increased ammonia load that is placed on the pond starting in spring.

Increasing Fixed-Film Bacterial Growth in Ponds

Fixed-film nitrification (such as is found in trickling filters) is more efficient and less susceptible to cold temperature wash-out of bacteria. There are floating blocks of bacterial growth media that can be installed in ash ponds to promote growth of fixed-film bacteria. These can be aerated to promote aerobic growth, or left unaerated to promote anoxic growth (denitrification). The use of these floating media should be investigated to determine their potential for nitrification (aerobic) and denitrification (anoxic) treatment.

Combining Ash Ponds and Wetlands

Ash ponds are optimal for removal of suspended solids into an ultimate disposal area. They are not optimal for biological treatment. Fixed-film processes can provide biological treatment in a compact volume. Wetlands are a natural form of fixed-film biological treatment. A settling ash pond could be followed by wetlands treatment. Vertical flow wetlands take advantage of the surface area of the underground media for bacterial growth. Downflow vertical wetlands can be alternately flooded and drained to provide for aerobic treatment (nitrification) in the media. If total nitrogen removal is required, the downflow vertical wetlands could be followed by flooded wetlands. Flooded wetlands can be used to grow and decay plants, producing anoxic conditions for denitrification (as well as reduction and removal of selenium) in subsequent upflow vertical wetlands. These could be followed by a final polishing pond, which provides for settling of solids and aerobic treatment of residual organics. The polishing pond could be enhanced by adding one or more aeration/mixers.

These natural wetlands technologies should be investigated as a simple and natural way of enhancing the capabilities of ash ponds to remove TSS as well as ammonia, total nitrogen and selenium.

6
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