Identification of Potential Concerns Associated with FDOT Use of Ammoniated Fly Ash

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Disclaimer

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the State of Florida Department of Transportation.

SI* (Modern Metric) Conversion Factors

Approximate Conversions to SI Units

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
AREA				
in^2	squareinches	645.2	square millimeters	mm^2
ft^2	squarefeet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: volumes greater than 1000 L shall be shown in m^3				

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
TEMPERATURE (exact degrees)				
^{o}F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^{o}C

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

Approximate Conversions to SI Units

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
AREA				
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
TEMPERATURE (exact degrees)				
^oC	Celsius	1.8C+32	Fahrenheit	^oF

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ILLUMINATION				
lx	lux	0.0929	foot-candles	fc
cd/m^2	$candela/m^2$	0.2919	foot-Lamberts	fl

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
FORCE and PRESSURE or STRESS				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

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16. Abstract

The objectives of this project were to identify potential concerns of using ammoniated fly ash in concrete and to provide recommendations for appropriate limits based on considerations of worker health and safety. A series of laboratory-scale exposure and leaching experiments with fly ash of different ammonium contents added into concrete were carried out to determine the mass transfer rates of ammonia/ammonium release from concrete to water/air. The measured mass transfer rates were applied in the semi-infinite diffusion model to assess maximum potential exposure for typical concrete handling scenarios. In overall consideration of modeling results, industry assessment, and results of previous research, a threshold of ammonium concentration in fly ash of 100 ppm was proposed for normal working conditions. However, the research team also recommended that appropriate safety protocols should be evaluated for some working conditions with poor ventilation.

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Executive Summary

Ammoniated Fly Ash

In recent years, coal-fired power plants are more frequently utilizing air pollution control technologies that result in fly ash with elevated concentrations of ammonia (referred to herein as ammoniated fly ash, AFA). Uncertainty exists regarding the potential implications of AFA when used in FDOT construction projects. The Hinkley Center for Solid and Hazardous Waste Management (the Center) and the Department of Environmental Engineering Sciences at the University of Florida (UF-EES) conducted research to identify potential concerns of AFA use and to provide recommendations for appropriate limits based on consideration including worker health and safety, chronic exposure concerns, nuisance odor problems, and product performance issues.

Ammonia is considered a high health hazard because it is corrosive to the skin, eyes, and lungs. Exposure to 300 ppm is immediately dangerous to life and health. It can explode if released in an enclosed space with a source of ignition present. OSHA's TWA-PEL (time-weighted average-permissible exposure limit) is 50 ppm, while NIOSH's REL (recommended exposure limit) is 25 ppm for 8-hr TWA and 35 ppm for 15-min. Ammonia has a low odor threshold of 20 ppm, so most people will seek relief from the pungent odor at low concentrations.

Since coal fly ash is routinely used as a cement substitute, the impact of ammonia presence in AFA must be considered. This research included a careful examination of the issues surrounding high ammonia content in cement due to the use of ammoniated fly ash. The research team was charged by the FDOT to provide recommendations for appropriate limits on the ammonia concentration in fly ash used as an admixture in concrete based on considerations including worker health and safety, chronic exposure concerns, and nuisance odor problems.

This report presents conclusions based on the research team's activities which included: laboratory experiments; contaminant transport and fate modeling; review of current literature. Additionally, through communications with power companies, the ash beneficiation industry (those facilities removing ammonia from fly ash), the concrete and cement industries, and with government transportation department officials pertinent information and guidelines have been included in the ultimate recommendations. Through this research the following conclusions were drawn.

> Exposure assessment modeling for scenarios where concrete was poured in an indoor setting showed that if a minimum ventilation rate was maintained, ammonia concentrations of 50 ppm in fly ash would not exceed the NIOSH recommended exposure level in air of 25 ppm. However, the exposure assessment modeling also showed that under some scenarios (e.g., poorly ventilated environments such as one that might occur inside the drum of a mixing truck and at the bottom of a high-walled form with a continuous pour of concrete), ammonia concentrations to which a worker would be exposed could exceed safe levels even if ammonia concentrations in fly ash were less than 100 ppm.

The leaching assessment of ammonia from hardened concrete samples made using ammoniated fly ash found that risk to public health or to the environment will not occur as a result of ammonia release from ammoniated concrete if fly ashes with an ammonia concentration less than 800 ppm are used.

There is a very clear and pressing need for a simple standardized testing protocol that can be used by all of the parties involved in this industry (producers, conditioners and users of ammoniated fly ash) to quickly, accurately, easily, and affordably determines the ammonia concentration in the fly ash. Further research is needed to specify such an assay.

The research team recommends that if FDOT chooses to specify an upper limit to the ammonia concentration in fly ash used for concrete production, 100 ppm would be protective of human health for most situations and would be achievable by vendors in the State of Florida using current ash treatment practices. The authors recommend, however, that under conditions where poor ventilation might occur, appropriate safety protocols should be evaluated by a trained professional (e.g., certified industrial hygienist) prior to job commencement so that necessary safety measures and/or job-specific ammonia concentration limits are used. Job managers should also be aware that even with the utilization of a 100 ppm ammonia limit in fly ash, the occurrence of ammonia odors may not be eliminated.

Table of Contents

List of Tables

List of Figures

Acronyms

AASHTO	American Association of State Highway and Transportation Officials
ACH	Air Changes per Hour
ACI	Activated Carbon Injection
AFA	Ammoniated Fly Ash
AGC	Annual Guideline Concentrations
APCD	Air Pollution Control Device
ASHRAE	American Society of Heating, Refrigeration, and Air Conditioning Engineers
ASR	Alkali Silicate Reaction
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CAIR	Clean Air Interstate Rule
CDC	Center for Disease Control
CTM	Conditional Test Method
DAF	Dilution Attenuation Factor
DI	Deionized
DWEL	Drinking Water Equivalent Level
EPA	Environmental Protection Agency
ESP	Electrostatic Precipitator
F.A.C.	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
FGC	Flue Gas Conditioning
FGD	Flue Gas Desulfurization
FIPR	Florida Institute of Phosphate Research
GCTL	Ground Water Cleanup Target Level
HDPE	High Density Polyethylene
IC	Ion Chromatography
IDLH	Immediately Dangerous to Health and Life
IFAS	Institute of Food and Agricultural Sciences
JEA	Jacksonville (FL) Electric Authority
LNB	Low NOx Burner
LOAEL	Lowest Observable Adverse Effect Level
LOI	Loss on Ignition
LS	Liquid to Solid Ratio
LSa	Liquid to Surface Area Ratio
MCL	Maximum Contaminant Level
MRL	Minimum Risk Level
NIOSH	National Institute of Occupational Safety and Health
NOAEL	No Observable Adverse Effect Level
NO_x	Nitrogen Oxides, i.e., NO and NO_2
OSHA	Occupation Safety and Health Association
PEL	Permissible Exposure Limit
PEL	Permissible Exposure Limit
RAP	Released Ammonia Percent
REL	Recommended Exposure Limit

RfC	Inhalation Reference Concentration
S/S	Solidification/Stabilization
SCR	Selective Catalytic Reduction
SCTL	Soil Cleanup Target Level
SJRPP	St. John’s River Power Park
SNCR	**Selective Non-**Catalytic Reduction
SPLP	Synthetic Precipitation Leaching Procedure
STEL	Short Term Exposure Limit
SWCTL	Surface Water Cleanup Target Level
TC	Toxicity Characteristic
TWA	Time Weighted Average
UF	University of Florida
UKY	University of Kentucky
USGS	United States Geological Survey
VDOT	Virginia Department of Transportation
W/CM	Water to Cementitious Material Ratio
ZHE	Zero Headspace Extractor

1. Introduction

In recent years, coal-fired power plants are more frequently utilizing air pollution control technologies that result in fly ash with elevated concentrations of ammonia (referred to herein as ammoniated fly ash, AFA). Uncertainty exists regarding the potential implications of AFA when used in FDOT construction projects. Concerns about AFA use have been raised, and science-based recommendations for appropriate limits based on considerations including worker health and safety, chronic exposure concerns, and nuisance odor problems need to be developed.

To meet regulatory mandates for nitrogen oxide (NO_x) control, coal-fired power plants often employ a technology known as selective catalytic reduction (SCR) to mitigate NO_x emissions. In the SCR process, ammonia is injected into the combustion exhaust prior to a catalytic reactor where the ammonia reacts with the NO_x to form nitrogen gas. Usually, when the SCR unit is staged upstream of the particulate control devices (e.g., baghouses or ESPs), excess unreacted ammonia will be captured with the fly ash in the particulate control device. Additionally, ammonia injection is commonly used to improve particulate collection in air pollution control devices. This process is referred to as flue gas conditioning and has an added benefit of reducing plume opacity.

Ammonia is considered a high health hazard because it is corrosive to the skin, eyes, and lungs. Exposure to 300 ppm is immediately dangerous to life and health. Ammonia can explode if released in an enclosed space with a source of ignition present. OSHA's TWA-PEL (time-weighted average-permissible exposure limit) is 50 ppm, while NIOSH's REL (recommended exposure limit) is 25 ppm for 8-hr TWA and 35 ppm for 15-min. Ammonia has a low odor threshold of 20 ppm, so most people will seek relief from the pungent odor at low concentrations.

Since coal fly ash is routinely used as a fractional cement substitute in concrete mixes, the impact of ammonia presence in AFA must be considered. Several concerns related to AFA use have been raised recently, including: (1) off-gassing of ammonia from AFA during various phases of handling and use and from the resulting AFA concrete; (2) worker health and safety due to the exposure to released ammonia, acute and chronic; and (3) nuisance odor. To ensure the health and safety of workers at DOT projects, research needs to be conducted to identify safe thresholds of ammonia loading in fly ash. Exposure routes and factors that affect ammonia discharge patterns and rates also need to be identified.

The Hinkley Center for Solid and Hazardous Waste Management and the Department of Environmental Engineering Sciences at the University of Florida were contracted to assist FDOT to identify potential concerns of AFA use and to provide recommendations for appropriate limits based on considerations including worker health and safety, chronic exposure concerns, and nuisance odor problems. This project was conducted in two phases. In Phase I, existing knowledge on the subject from the scientific literature, the regulatory community, and stakeholders was gathered and synthesized. Phase I also included conducting a basic mass balance assessment to determine whether further research was warranted to better quantify potential ammonia emissions and worker exposure, and development of methodology for such research. The results of Phase I prompted initiation of Phase II of the project, the focus of which was laboratory testing in support of recommendations for ammonia concentration restrictions for fly ash used in FDOT construction projects.

This report presents the results of both Phases I and II of the research. As part of Phase I, the researchers gathered information from published material and considered policies and practices in other states (Chapter 2 – Literature Review), and conducted a survey of current or past experience of other state DOTs regarding the AFA issues (Chapter 3 – State Transportation Department Survey). The current regulatory limits for worker safety and environmental health with respect to ammonia/ammonium exposure or release were reviewed and summarized (Chapter 4 – Regulatory Review). The current use of ammonia injection at coal-fired units was reviewed and summarized, and the coal ash and cement industries in Florida were queried for their current knowledge and experience with AFA (Chapter 5 – Industry Review). This information was used to estimate the range of potential ammonia exposure to workers as a function of the amount of ammoniated fly ash used and its respective ammonia concentration (Chapter 6 – Preliminary Assessment of Potential Ammonia Release).

The information gathered in Phase I suggested that exposure to ammonia could be an issue under plausible use scenarios, and thus experimental studies were initiated to determine an appropriate threshold(s), i.e., ammonia concentration in fly ash, that FDOT can establish for use of ammoniated fly ash used under different conditions (Phase II). A series of laboratory-scale experiments were conducted using ammoniated fly ash at different ammonia concentrations in concrete mixes and the ambient ammonia concentrations released were evaluated in different media, i.e. air and water; these methods are outlined in detail in Chapter 7. The results of these experiments are summarized in Chapter 8, with these results in turn being used to model different potential exposure scenarios and make the appropriate recommendations in Chapter 9. The report ends with Chapter 10 – Summary and Conclusions. Data and experimental details are included in a series of appendices.

2. Literature Review

2.1. Coal Fly Ash Background

Coal fly ash is produced from the combustion of pulverized coal for electricity generation. The composition of coal fly ash by coal type can be seen in Table 1. Fly ash is carried with the flue gas from the boiler to where it is collected in the baghouse or electrostatic precipitator. Fly ash is composed mostly of silica with nearly all particles spherical in shape. Fly ash is a pozzolan, a siliceous material which in the presence of water will react with calcium hydroxide at room temperature to produce cementitious compounds, e.g. see Equation 1.

$$\mathrm{Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2H_2O} \qquad (1)$$

Because of its spherical shape and pozzolanic properties, fly ash is useful in cement and concrete applications. Fly ash has been used in the past as an additive, feedstock or component of concrete products, grout, cement, filler material for structural applications and embankments, waste stabilization and/or solidification, soil modification and/or stabilization, flowable fill, road bases, sub-bases, pavement, and mineral fill in asphalt (US-EPA, 2011a).

Table 1: Composition by Percentage of Coal Fly Ashes by Coal Source (US-EPA, 2011a)

Component	Bituminous	Sub-bituminous	Lignite
SiO_2	20 - 60	40 - 60	15 - 45
Al_2O_3	5 - 35	20 - 30	10 - 25
Fe_2O_3	10 - 40	4 - 10	4 - 15
CaO	1 - 12	5 - 30	15 - 40
MgO	0 - 5	1 - 6	3 - 10
SO_3	0 - 4	0 - 2	0 - 10

2.2. Fly Ash Classifications

By the American Society for Testing and Materials (ASTM) definitions, specifically ASTM C618, there are two classes of fly ash, Class C and Class F, which can be used as additives in the production of Portland cement or as a partial replacement of Portland cement in concrete mixtures (ASTM, 2010). These classes of fly ash differ in silica, alumina, and iron oxide content. Class F fly ash should have a combined silica, alumina, and iron oxide content equal to or greater than 70% wt. while Class C fly ash should have a combined silica, alumina, and iron oxide content between 50 – 70% wt. (ASTM, 2010). These constituent concentrations are largely influenced by the chemical composition of the coal, i.e. bituminous or sub-bituminous coal, burned to produce them. The state of Florida produces Class F fly ash in abundance and this is the primary class of fly ash added to concrete mixtures in the state; however, some Class C fly ash is utilized as well. Additionally, to meet these standards the fly ash must have a fineness of 45 μm or less and have a loss-on-ignition (LOI) of less than 6%. Class F fly ash is typically produced from bituminous coal and rarely exhibits cementitious properties when mixed alone with water. Conversely, Class C fly ash is typically produced from sub-bituminous coal and exhibits pozzolanic activity when mixed with water. It should be noted that not all fly ashes meet the ASTM C618 definitions and these definitions do not contain environmental regulations.

2.3. Fly Ash Production and Use

In 2009, approximately 9.8 million tons of coal fly ash was used in the production of Portland cement concrete (ACAA, 2009). The addition of coal fly ash to Portland cement concrete (PCC) improves its workability, reduces segregation, bleeding, heat evolution and permeability, inhibits alkali-silica reactions and enhances sulfate resistance as well as reducing costs and increasing beneficial reuse (US-DOT, 2011). Fly ash improves workability mainly because of the spherical shape of the fly ash particulate. The fly ash exhibits a “ball bearing” character which lends itself to the cement paste to produce a product that is easier to apply. Segregation and bleeding of binder materials from aggregate in concrete is reduced with the addition of fly ash because of its fineness and uniformity. It should be noted that the original motivation for including fly ash in cement was because of its slower reaction rate and therefore slower heat evolution. This slower heat evolution is desirable when a very large concrete structure is built, e.g. Hoover dam, because internal heating can become dangerous to the structural integrity of the concrete. The addition of Class F fly ash can reduce the prevalence of alkali- silica reactions. However, care must be taken with the addition of Class C fly ash since it can sometimes contain alkali metals and can actually increase the alkali-aggregate reaction. The alkali-aggregate reaction occurs over time in concrete between the highly alkaline cement paste and reactive non-crystalline (amorphous) silica, which is found in many common aggregates. The alkali-aggregate reaction is the same as the Pozzolanic reaction but in the opposite direction of Equation 1 (US-DOT, 2011).

By forcing the Pozzolanic reaction in reverse, a swelling gel of $H_2SiO_4^{2-}$ and alkali metals is produced which causes cracking in the concrete. Sulfate resistance refers to the resistance of the concrete to the transport of sulfate through its pore structure. This influx of sulfate can cause the in situ production of ettringite which swells inside the concrete structure. Resistance to the flux of sulfate will result in reducing the cracking due to this expansion. This is similar to the alkali-aggregate reaction previously mentioned (US-DOT, 2011). Again, it should be noted that fly ash characteristics vary between different sources. This fact will be highlighted in the next section, with respect to ammonia concentrations, for ammoniated fly ash (AFA).

2.4. Ammoniated Fly Ash Production

Recent changes to regulations, in the form of the 2005 Clean Air Interstate Rule (CAIR; 40 CFR Parts 51, 72, 73, 74, 77, 78 and 96), of acid rain precursors, i.e. NO_x and SO_x, have affected the quality and composition of coal fly ash (FDEP, 2009; Kosson et al., 2009; Rathbone and Robl, 2003). Typical changes to fly ash quality are an increase in ammonia content and carbon content. Carbon content corresponding to an LOI of greater than 6% should not be used in the production of Portland cement (ASTM, 2010).

The increased ammonia concentration has led to a concern over the health and safety of workers using cement/concrete amended with ammoniated fly ash (Rathbone and Robl, 2003). One ash processing company (Separation Technologies, LLC) states that, as an industry standard, fly ash with ammonia concentrations greater than 100 mg/kg (ppm) is unmarketable (Bittner et al., 2009). Meanwhile, the Rathbone and Robl, 2003 study indicated that ammonia concentrations released to the air from ammoniated fly ash could be as high as 200 ppm if there was adequate ventilation.

2.5. Changes to NO_x Controls and Ammonia Adsorption on Fly Ash

Low NO_x burners (LNB), Selective Catalytic Reduction systems (SCR) and Selective Non-Catalytic Reduction systems (SNCR) have been installed at many coal power plants to meet the NO_x reduction required in the CAIR standards. These changes have resulted in higher concentrations of ammonia adsorbed to the fly ash and/or lower boiler temperatures which result in residual unburned carbon in the fly ash (FDEP, 2011; Kosson et al., 2009; Rathbone et al., 2003).

The changes in the quality of fly ash could lead to a shortage of appropriate fly ash for use as a pozzolan in cement production (Bittner et al., 2009). SCR and/or SNCR systems used for post-combustion NO_x control can increase the amount of ammonia in the flue gas due to ammonia slip, i.e. unreacted ammonia from the NO_x reduction reaction. Additionally, ammonia can be deposited on fly ash from ammonia injection for flue gas conditioning (FGC) prior to the particulate controls. The degree to which ammonia is deposited is dependent on the SO_3 content, fly ash sulfur content, alkalinity of the fly ash, the ammonia concentration in the flue gas and the ash loading in the flue gas (Bittner et al., 2009).

The addition of ammonia for NO_x controls can result in fly ashes with 200 – 2500 ppm concentrations (Bittner et al., 2009). The ratio of the concentration of ammonia adsorbed to the fly ash and the concentration in the flue gas has been reported to be approximately 50:1 (Bittner et al., 2009). This result means that flue gas ammonia concentrations, i.e. ammonia slip, higher than 2 ppm would likely result in an unmarketable fly ash, i.e. > 100 ppm ammonia concentration in the fly ash. The maximum permissible limit of ammonia slip in most SCR systems, i.e. 2 ppm, is below the typical levels seen in all of the alternative NO_x post-combustion controls: FGC (50 ppm in flue gas/2500 ppm in fly ash), SNCR (5 – 20 ppm in flue gas/250 –

1000 ppm in fly ash) and SCR (0 – 5 ppm in flue gas/0 – 250 ppm in fly ash) (Bittner et al., 2009). In another study conducted by PMI, Inc., the concentration of ammonia in fly ash from SCR was generally found to be 60 ppm, while AFA from SNCR was in the 230~735 ppm range (Giampa, 1999). This result agrees closely with the predictions made by Bittner et al., 2009.

2.6. Leaching Characteristics of Ammoniated Fly Ash

It should be noted that studies have been conducted on the leaching of ammonia from coal fly ash and the effect of ammonia concentration has on the leaching characteristics of particular elements, e.g. Hg, Cd and Cu; however, there has not been adequate investigation of the effects of ammonia concentrations on the solidification/stabilization of contaminants in concrete and cement amended with coal fly ash. Please note that the investigation of metals leaching as a result of increased ammonia concentration in the fly ash is beyond the scope of this project.

One study found that ammonia was adsorbed on fly ash as one of two salts, ammonium bisulfate and ammonium sulfate, when sulfur is present in the flue gas. Additionally, it was found that there was no significant difference between the leaching behaviors of these two salts. Ammoniated fly ash was exposed to deionized water for various intervals and the extracted ammonia mass was measured after each exposure interval. It was shown that approximately 85% of the initial ammonia was leached in the first ten minutes and 99% of the initial ammonia was leached after one hour of exposure to deionized water (Wang et al., 2002). It is clear that the ammonium salts absorbed onto the surface of the fly ash is highly soluble and can be reliable leached from the fly ash surface by “washing” with deionized water.

2.7. Conclusions

Based on the previously mentioned data and studies, the following conclusions can be drawn. Following the installation of NO_x control technology at coal-fired power plants, there has been an increase of ammonia adsorbed onto the fly ash captured in the baghouses or electrostatic precipitators (ESP). The concentration of ammonia adsorbed onto the fly ash is variable between facilities, air pollution control technology and management practices but generally ranges between 50-3000 ppm. It is unclear if these concentrations of ammonia adsorption onto fly ash are at levels that could potentially expose workers, the public or the environment to unsafe levels of ammonia. Based on the literature review a list of researchers and institutes previously and currently researching the production, characterization, disposal and reuse of AFA has been compiled in Table 2 below.

However, it should be noted that only the work by Rathbone et al., 2003, reported studies directly related to the reuse of AFA in cement and/or concrete and potential exposure to ammonia. It should be noted however, in the work by Rathbone et al., 2003, only stationary ambient concentrations were measured, not personal exposure levels. EPA and ASTM methods were used instead of OSHA or NIOSH methods. Aside from ventilation, the effects of important environmental parameters, e.g. mobility of contaminants, were not examined. Additionally, the impact on concrete performance was not investigated.

In summary, it is not clear if levels of ammonia volatilized from concrete amended with AFA will reach unsafe levels. A clear relationship should be drawn between ammonia adsorbed onto fly ash and possible exposure since ammonia levels in fly ash will vary between facilities. Additionally, the working conditions, e.g. ventilation and temperature, where the concrete is poured will have an effect on the exposure of workers and needs to be better quantified.

Table 2: List of Researchers and Institutes Previously and Currently Researching AFA

Name	**Institute/Company**	**Research**
Robert Rathbone	University of Kentucky	Characterization
Robert Hurt	Brown University	Characterization and removal
Jay R. Turner	Washington University, St. Louis	Adsorption mechanism
Lamar Larrimore	Southern Company	Characterization
Hao Wang	University of Alabama	Leaching
Carol Cardone	Department of Energy	Characterization
Henry Liu	Freight Pipeline Company	Leaching
Jianming Wang	University of Missouri-Rolla,	Leaching
Vincent M Giampa	Progress Materials, Inc.	Control
D. Kosson	Vanderbilt University	Leaching
Anthony Palumbo	Oak Ridge National Laboratory	Leaching

3. DOT Nationwide State Department Survey

3.1. Survey Objectives and Methodology

Every state transportation department was contacted to determine their current practices of coal fly ash use in concrete. Additionally, a survey of their level of awareness of AFA use in concrete and their experience with this issue was determined. Finally, any investigations conducted or sponsored by state DOTs were requested. To expedite communication about these issues between state DOTs, a survey was drafted by the Hinkley Center and the University of Florida and was distributed to all states. The survey can be seen in Appendix I; however, the questions are listed below in Table 3 as they appeared in the survey. The current fly ash specification for use in concrete products enforced by state DOTs can be seen in Table 4 below. In Table 5, contact information for representatives and knowledgeable technicians can be found for reference. All other survey responses can be found in Table 6, below.

3.2. Results of Survey

Current responses, 18 states and one Canadian territory, to this survey indicated that there was limited awareness of ammonia content in fly ash. No other official DOT investigations into this issue had been conducted, with the exception of Virginia. While the contact at VDOT did not specifically cite a study, he conveyed that there was investigation into ammoniated fly ashes in the mid-1990s. According to VDOT, the study concluded that ammonia did not represent a danger to workers or to concrete quality.

Currently, the Missouri Department of Transportation is the only state DOT that has a limit on ammonia concentration in fly ash used in state projects. The contact at the Missouri Department of Transportation stated that they currently limit the ammonium concentration of fly ash used in DOT construction to less than 100 ppm. This statement was followed up by contacting Mr. Sam Marshall (Missouri DOT) and inquiring about this limit. Mr. Marshall stated that this limit is not currently written into any regulation but is a “rule of thumb” developed by the Missouri DOT through conversations with industry and customers. He also stated that fly ash with ammonium levels higher than 100 ppm would be unmarketable due to ammonia odor complaints.

Table 3: Survey of State DOTs

Question Number	**Question**
1	Is fly ash from the combustion of coal used in the production of cement or concrete in your state?
2	Is high ammonia in concrete (due to fly ash addition) a concern in your state?
3	Have you had complaints, issues, or questions about ammonia as it relates to concrete? If so, from what industries, or other sources?
4	Does your agency enforce or recommend any specifications regarding fly ash in cements or concrete? If so, please elaborate.

Table 3 Continued: Survey of State DOTs

5	Does your agency enforce or recommend any specifications regarding ammonia in fly ash, cement, or concrete? If so, please elaborate.
6	What actions (research, regulations, etc.) in your state have been taken to address the ammoniated fly ash issue?
7	We would greatly appreciate the contact information of someone in your state who is experienced with these issues. Please list their information below.

Table 4: List of Fly Ash Specifications Enforced by State DOTs for Use in Concrete

State DOT	**State Specification**
Georgia	AASHTO M295
Kentucky	Kentucky Method 64-325/R ratio ASTM C618
Missouri	ASTM C311; AASHTO M295
Texas	ASTM C618
Washington	Maximum 35%
New Jersey	ASTM C618
Ohio	ASTM C618
Kansas	ASTM C311
Maryland	No
Iowa	No response to question
South Carolina	AASHTO M295
Vermont	Yes, clarification needed
New York	AASHTO M295 (with optional chemical requirements)

Table 4 Continued: List of Fly Ash Specifications Enforced by State DOTs for Use in Concrete

Montana	Only maximum percentage replacement allowed with loss on ignition specifications.
Utah	Agency requires a minimum of 20% (maximum 30%) fly ash content in concrete mix designs unless it can be shown that ASR concerns can be mitigated without fly ash.
Virginia	AASHTO M 295 and M 240
Saskatchewan	None
Illinois	Follows AASHTO Standards, did not reference specific sections.
Minnesota	Tests fly ash based on a 48 hour production, for LOI, fineness, specific gravity and soundness tests.

Table 5: Contact Information for State DOT Specialists on Fly Ash Use in Concrete

State	Contact	Email	Tel
Georgia	Myron K. Banks	mbanks@dot.ga.gov	404-608-4876
Kentucky	Ted Web	Ted.Webb@ky.gov	502-564-3160
Missouri	Sam Marshall	Robert.marshall@modot.mo.gov	573-526-5855; 573-690-9986
Kansas	Rodney Montney	Rodney@ksdot.org	785-291-3841
Maryland	Dan Sajedi	dsajedi@sha.state.md.us	443-572-5162
Iowa	Todd Hanson	Todd.hanson@dot.iowa.gov	515-239-1226
Texas	Andy Naranjo	Andy.naranjo@txdot.gov	512-506-5849
Washington	Kurt Williams	willikr@wsdot.wa.gov	360-709-5410
New Jersey	Fred Lovett	Fred.lovett@dot.state.nj.us	609-530-5148
Ohio	Bryan Struble	Bryan.struble@dot.state.oh.us	614-275-1325
South Carolina	Melissa L. Campbell	campbellml@scdot.org	803-737-1195
New York	Daniel Dennis	ddennis@dot.state.ny.us	518-457-9798
Vermont	William Ahearn	bill.ahearn@state.vt.us	802-828-2561
Montana	Matt Needham	maneedham@mt.gov	406-444-7260
Utah	Bryan Lee	bryanlee@utah.gov	801-965-3814
Virginia	Michael M. Sprinkel	michael.sprinkel@vdot.virginia.gov	434-293-1941
Saskatchewan	Len Frass	len.frass@gov.sk.ca	306-933-5226
Minnesota	Bernard I. Izevbekhai	bernard.izevbekhai@state.mn.us	651-366-5454
Illinois	Douglas A. Dirks	Douglas.Dirks@illinois.gov	217-782-7208

Table 6: Responses to DOT Survey

Question Number as Listed in the Survey							
State	**1**	**2**	**3**	**4**	**5**	**6**	**7**
GA	Yes	No	No	See Table 6	No	No	See Table 7
KY	Yes	No	No	See Table 6	No	No	See Table 7
MO	Yes	No	No	See Table 6	No	<100 ppm	See Table 7
KS	Yes	No	No	See Table 6	No	No	See Table 7
MD	Yes	No	No	See Table 6	No	No	See Table 7
IA	No	No	No	See Table 6	No	No	See Table 7
TX	Yes	No	No	See Table 6	No	No	See Table 7
WA	Yes	No	No	See Table 6	No	No	See Table 7
NJ	Yes	No	No	See Table 6	No	No	See Table 7
VT	Yes	No	No	See Table 6	No	No	See Table 7
NY	Yes	No	No	See Table 6	No	No	See Table 7
SC	Yes	No	No	See Table 6	No	Monitoring actions of other states	See Table 7
OH	Yes	No	No	See Table 6	No	No	See Table 7
MT	Yes	No	No	See Table 6	No	Not at present	See Table 7

Table 6 Continued: Responses to DOT Survey

Question Number as Listed in the Survey							
State	**1**	**2**	**3**	**4**	**5**	**6**	**7**
UT	Yes	No	No	See Table 6	No	No	See Table 7
VA	Yes	No	Yes, but no recent issues	See Table 6	No	Not at present	See Table 7
SK (Canada)	Yes	No	No	See Table 6	No	No	See Table 7
IL	Yes	No	No	See Table 6	No	No	See Table 7
MN	Yes	No	No	See Table 6	No	No	See Table 7

4. Ammonia Regulatory Review

4.1. Health and Environmental Effects

Ammonia (NH_3) is a skin, eye and respiratory tract irritant in both its gaseous and liquid (aqueous solution) forms due to its alkaline nature. Exposures to levels exceeding 50 ppm in air can result in immediate irritation to the nose and throat. Exposure to a concentration of 250 ppm is bearable for most people only for 30 – 60 minutes. Exposure to levels greater than 300 ppm can cause chemical burns to the eyes, skin and respiratory tract (US-HHS, 2004).

Additionally, it is well known that ammonia is toxic to fish and other aquatic organisms. In a paper by Francis-Floyd, R. et al., 1996, it was stated that, of all the water quality parameters that affect fish, ammonia is the most important after oxygen, especially in intensive systems. Ammonia, even in small amounts, causes stress and damages gills and other tissues. Unionized ammonia can be toxic to aquatic life at a concentration as low as 0.05 mg/L, while ionized ammonia is 100 times less toxic than unionized ammonia, i.e. approximately 5 mg/L (Francis-Floyd, R. et al., 1996).

4.2. Regulations – Air

Ammonia exposure guidelines and limits for various regulatory agencies are listed in Table 7. Guidelines set by several state agencies are listed in Table 8 (OEHHA, 1998 and OME, 2011). These guidelines are derived from the Minimal Risk Level (MRL) set by the Agency for Toxic Substances and Disease Registry (ATSDR) of the Centers for Disease Control (CDC) and the Inhalation Reference Concentration (RfC) set by the EPA. The ATSDR derives their MRLs from the Lowest Observable Adverse Effect Level (LOAEL) and the No Adverse Effect Level (NOAEL) which are determined through epidemiological studies. Additionally, the EPA derives its RfC for ammonia from the NOAEL using an uncertainty factor of 10 to protect sensitive individuals and 3 for data base deficiencies (FDEP, 2005). The RfC is an estimate of a daily inhalation exposure of a human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (FDEP, 2005).

It should be noted that the EPA does not currently define an oral reference dose for ammonia. Due to this fact, the FDEP derives its oral reference dose and inhalation reference dose based on the EPA RfC and the ATSDR MRL, and the assumptions that an individual has a mass of 70 kg and breathes a volume of 20 m^3/day of air. Therefore, using these assumption and EPA's RfC an inhalation reference dose of 0.03 mg/kg-day is calculated. Likewise, the oral reference dose is calculated with the same assumptions but based off the MRL for ammonia.

Table 7: Air Exposure Limits and Guidelines for Ammonia from Various Regulatory Agencies (FDEP, 2005)

Regulatory Agency	Description	Guideline or Standard
EPA	RfC	0.14 ppm
	NOAEL	9.2 ppm
	LOAEL	25 ppm
NIOSH	REL	25 ppm
	STEL	35 ppm
	IDLH	300 ppm
OSHA	PEL	50 ppm

The RfC for ammonia from the US EPA has been referenced by other state agencies to derive their own air quality guidelines. The state agencies, listed in Table 10, include California, Massachusetts, Michigan and New Jersey. The air guidelines of New York State were derived from occupational exposure limits. The California EPA has a revised acute Reference Exposure Level of 3200 $\mu g/m^3$ based on the eye and respiratory irritations on humans. In addition, California and New York have developed short-term (1-hour) air guidelines in addition to their annual criteria. The State of California derived its acute reference value of 3200 $\mu g/m^3$ based on dose response data for human respiratory irritation, using the methodology proposed by Industrial Biotest Laboratories, 1973; MacEwen et al., 1970; Silverman et al., 1949; and Verberk, 1977.

As shown in Table 7, OSHA Permissible Exposure Limit (PEL) for general industry and maritime are both 50 ppm, while American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) and National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) are both 25 ppm. NIOSH set the Immediately Dangerous to Life or Health Concentration to be 300 ppm.

Table 8: Existing Air Quality Guidelines of Other State Agencies for Ammonia

Agency	Guideline Value*	Basis of Guideline	Comments
California	200 µg/m^3 (chronic annual)	US EPA RfC	NOAEL (HEC) adjusted with uncertainty factors,
	2100 µg/m^3 (acute 1-h reference exposure level);	Human respiratory irritation concentration	Noncancer chronic Reference Exposure Level
	Proposed acute REL: 3200 µg/m^3	Eye and respiratory irritations in humans	Noncancer chronic Reference Exposure Level
Massachusetts	100 µg/m^3 (annual average ambient level)	US EPA RfC	Allowable Ambient Limit
	100 µg/m^3 (24-hour ceiling limit)	US EPA RfC	Threshold effects exposure limit
Michigan	100 µg/m^3 (24-hour average)	US EPA RfC	Screening level
New Jersey	100 µg/m^3 (24-hour average)	US EPA RfC	Ambient annual guideline concentration
New York	360 µg/m^3 (annual; AGC)	Occupational exposure limits; US EPA	Chronic annual guideline
	4000 µg/m^3 (1-hour average; SGC)	Occupational exposure limits	Acute 1-hour average; ACGIH TLV-TWA

*Using conditions of 1 atmosphere and 20 °C, 1 ppm = 0.708 mg/m^3 (ATSDR, 1990). Various agencies use conversion factors based on a range of temperatures, varying between 0 °C to 25 °C. Depending on the selected temperature, conversion of units may vary slightly.

4.3. Regulations – Soil and Water

The Groundwater Cleanup Target Level (GCTL), the Soil Cleanup Target Level (SCTL), and the Surface Water Cleanup Target Level (SWCTL) are the most important limits when considering the leaching of ammonia from a material. Table 9 lists these levels. These reference doses are then used to calculate the Cleanup Target Levels (CTLs) based on Equations 2, 3, and 4, below. Furthermore, assumptions are made to consider exposure level for each of the CTLs. These assumptions, listed below in Table 10, are used to calculate the SCTL based on the exposure experienced by a resident or a worker. In the case of the resident, the maximum exposure is assumed to be the exposure experienced by a child, while worker exposure is based on assumptions surrounding adult exposure. For ammonia, the SCTL is set at 35,000 mg/kg for residential settings and 880,000 mg/kg for industrial settings. However, it should be noted that ammonia SCTLs are based on an inhalation reference dose and, therefore, the un-ionized NH_3 species concentration. This is significant because, as soil pH increases, the SCTL decreases due to increased volatilization of NH_3, as can be seen in Table 11. This phenomenon will be addressed in the mass balance assessment (Task 5) and the development of experimental methodology (Task 6).

Table 9: Soil, Surface water and Groundwater Cleanup Target Levels

Regulatory Agency	Description	Guideline or Standard
FDEP	SCTL	35000 mg/kg (Residential) 880000 mg/kg (Industrial)
	GCTL	2800 µg/L
	SWCTL	20 µg/L

GCTLs are standards set by the FDEP to protect human health from contaminants in groundwater. The GCTLs are either primary or secondary standards, based on the Florida Drinking Water Standards, Monitoring and Reporting (Chapter 62-550 F.A.C.), or minimum criteria concerning health considerations and aesthetic factors but are not listed in Chapter 62-550 F.A.C. In the case of ammonia, there is a 2.8 mg/L minimum criterion, which is calculated according to Equation 4 based on the values listed in Table 10. SWCTLs are criteria set by the FDEP to protect human health and aquatic life in surface waters. SWCTLs are either listed as standards from Surface Water Quality Criteria (Chapter 62-302 F.A.C.), which are based on risk associated with the consumption of fish or surface water, or are otherwise listed due to concern for human health, aquatic toxicity or nuisance control as toxicity criteria. A Surface Water Quality Criterion of 20 μg/L is listed for ammonia as total NH_3, i.e. NH_3 and NH_4^+ in solution (FDEP, 2005).

$$\mathrm{SCTL} = \frac{\mathrm{THI}\times\mathrm{BW}\times\mathrm{AT}\times\mathrm{RBA}}{\mathrm{EF}\times\mathrm{ED}\times\mathrm{FC}\times\left[\left(\frac{1}{\mathrm{RfD_0}}\times\mathrm{IR_0}\times10^{-6}\frac{\mathrm{kg}}{\mathrm{mg}}\right)+\left(\frac{1}{\mathrm{RfD_d}}\times\mathrm{SA}\times\mathrm{AF}\times10^{-6}\frac{\mathrm{kg}}{\mathrm{mg}}\right)+\left(\frac{1}{\mathrm{RfD_i}}\times\mathrm{IR_i}\times\left(\frac{1}{\mathrm{VF}}+\frac{1}{\mathrm{PEF}}\right)\right)\right]} \tag{2}$$

$$\mathrm{SWCTL}\left({}^{\mu\mathrm{g}}/_{\mathrm{L}}\right) = \frac{\mathrm{RfD_0}\times\mathrm{BW}}{\mathrm{FI}\times\mathrm{BCF}}\times\mathrm{CF} \tag{3}$$

$$GCTL\left({}^{\mu g}/_{L}\right) = \frac{RfD_0\times BW\times RSC\times CF}{WC} \tag{4}$$

Table 10: Default Values in the Calculation of the SCTL, GCTL and SWCTL (FDEP, 2005)

Symbol	**Definition**	**Receptor**	**Default**
BW	Body Weight (kg)	Aggregate resident	51.9
		Child	16.8
		Adult/Worker	76.1
IR_o	Ingestion Rate, Oral (mg/day)	Aggregate resident	120
		Child	200
		Adult/Worker	50
EF	Exposure Frequency (days/yr)	Aggregate resident	350
		Child	350
		Adult/Worker	250
ED	Exposure Duration (years)	Aggregate resident	30
		Child	6
		Adult/Worker	25
SA	Surface Area Exposed (cm^2/day)	Aggregate resident	4810
		Child	2960
		Adult/Worker	3500
AF	Adherence Factor (mg/cm^2)	Aggregate resident	0.1
		Child	0.2
		Adult/Worker	0.2

Table 10 Continued: Default Values in the Calculation of the SCTL, GCTL and SWCTL

Symbol	Definition	Receptor	Default
AT	Averaging Time (days) (carcinogens)	N/A	25550 (70 years)
	Averaging Time (days) (non-carcinogens)	Aggregate resident	10950 (30 years)
		Child	2190 (6 years)
		Adult/Worker	9125 (25 years)
IR_i	Inhalation Rate (m^3/day)	Aggregate resident	12.2
		Child	8.1
		Adult/Worker	20
DA	Dermal Absorption (unitless) (organics)	-	0.01
	Dermal Absorption (unitless) (inorganics)	-	0.001
VF	Volatilization Factor (m^3/kg)	-	chemical-specific
PEF	Particulate Emission Factor (m^3/kg)	-	1.24×10^9
TR	Target Cancer Risk (unitless)	-	10^{-6}
THI	Target Hazard Index (unitless)	-	1

Table 11: Changing Values of SCTLs with Variable pH (FDEP, 2005)

Soil pH*	Percent Un-Ionized Ammonia (NH3)	Residential (mg/kg)	Industrial (mg/kg)
	100	750	4000
9.5	64.3	1200	6200
8.5	15.2	4400	26000
7.5	1.77	19000	180000
6.5	0.18	32000	630000
6	0.0568	34000	780000
5.5	0.018	35000	840000
5.04**	0.00624	35000	860000
5	0.00569	35000	870000

* Increasing ammonia concentrations will tend to increase soil pH. Situations of low soil pH and high ammonia concentrations, while theoretically possible, are unlikely to exist at contaminated sites.

** Average pH of soils in Florida

4.4. Sampling and Analytical Methods

The detection and monitoring of ammonia can be accomplished in various ways, as can be seen in Table 12 below. Additionally, EPA CTM 027 describes a method for collecting and analyzing ammonia from stationary sources.

Table 12: Ammonia Collection and Analysis Methods

Application	Method Number	Method Title
Water and soil	EPA 349.0	Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis
	EPA 350.1	Determination of Ammonia Nitrogen by Semi-automated Colorimetry
	EPA 350.2	Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric Distillation Procedure)
	EPA 350.3	Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode)
	USGS I-2525	Nitrogen, Ammonia, Low ionic-strength water, Colorimetry, Salicylate-hypochlorite, Automated-segmented flow
	ASTM D1426	Standard Test Methods for Ammonia Nitrogen in Water
Air	OSHA ID-164	Ammonia in Workplace Atmospheres
	OSHA ID-188	Ammonia in Workplace Atmospheres - Solid Sorbent
	NIOSH 6016	Ammonia adsorb to sulfuric acid-treated silica gel, then analyze by IC

5. Industry Assessment

5.1. Coal Fly Ash in Florida

A list of currently operating coal-fueled power plants is provided below in Table 13. Additionally, each facility's current Air Pollution Control Devices (APCDs) are also listed. As can be seen, 12 of the 15 coal power plants currently inject ammonia for control of nitrous oxides. However, the list below does not indicate which facilities currently inject ammonia for flue gas conditioning purposes. Ammonia is injected directly before particulate control devices to control SO_3 (blue plume) emissions and to increase collection efficiency of particulates. Ammonia injection for flue gas conditioning represents the largest volume addition of ammonia to fly ash. Currently, it is known that Crystal River Power Complex was injecting ammonia for flue gas conditioning and recently halted injection. While Tampa Electric Company (TECO) is still injecting ammonia for flue gas conditioning and have plans to continue indefinitely.

Since it is not known which facilities may begin injecting ammonia for NO_x control or flue gas conditioning it is important to establish a limit on acceptable ammonia content. All fly ash should be tested for ammonia content as it leaves for reuse at ready-mix facilities.

Table 13: List of Coal-Fired Power Plants and Associated APCDs*

Plant	Facility ID	County	Unit	Add-on Controls
Progress Energy, Crystal River Plant	0170004	Citrus	1 and 2	ESP [a]
			4 and 5	LNB/SCR [b]/WFGD/AI/ESP[c]
Tampa Electric (TECO), Big Bend Station [k]	0570039	Hills-borough	1	ESP/WFGD (pre SCR)
			2	ESP/WFGD (pre SCR)
			3	LNB/ESP/SCR/WFGD
			4	LNB/ESP/SCR/WFGD
Orlando Utilities Commission (OUC) Stanton	0950137	Orange	1	LNB/ESP/WFGD
			2	LNB/ESP/SCR/WFGD

Table 13 Continued: List of Coal-Fired Power Plants and Associated APCDs*

Plant	Facility ID	County	Unit	Add-on Controls
Seminole Electric, Palatka	1070025	Putnam	1	LNB/ESP/SCR/WFGD/AI
			2	LNB/ESP/SCR/WFGD/AI
Gulf Power, Plant Crist	0330045	Escambia	4	LNB/ESP/SNCR[b]/WFGD
			5	LNB/ESP/SNCR/WFGD
			6	LNB/ESP/SNCR[c]/WFGD
			7	LNB/ESP/SCR/WFGD
Indiantown CoGeneration	0850102	Martin	1	LNB/SCR/SDA[e]/FF[a]
Gainesville Regional Utilities (GRU Deerhaven	0010006	Alachua	2	LNB (permitted)/SCR/DFGD[f]/FF
Lakeland Electric, C.D. McIntosh Plant	1050004	Polk	3	LNB/ESP/SCR/WFGD
JEA St. Johns River Power Park[k]	0310045	Duval	1 and 2	LNB/ESP/SCR/WFGD
JEA Northside Generating Station (CFB[g])	0310045	Duval	2 and 3	SNCR/$CaCO_3$[h]/CaO[i]/FF
Cedar Bay CoGen (CFB)	0310337	Duval	1,2 and 3	SNCR/$CaCO_3$/FF
Central Power and Lime	7774801	Hernando	1	Integration with Cement Plant[j]
Gulf Power, Plant Scholtz	0630014	Jackson	1 and 2	ESP
Gulf Power, Plant Lansing	0050014	Bay	1 and 2	ESP/LNB/SNCR

Table 13 Continued: List of Coal-Fired Power Plants and Associated APCDs*

Plant	Facility ID	County	Unit	Add-on Controls
TECO Polk IGCC [n]	1050233	Polk	1	Steam/N_2/Gas Cleanup
a.) ESP and FF mean electrostatic precipitator and fabric filter for particulate matter (PM) control. b.) SCR and SNCR mean selective catalytic and non-catalytic reduction for nitrogen oxides (NO_X) control. Most conventional coal-fueled plants also have Low NO_X burners (LNB) and some have overfire (OFA) air. c.) SCR will be installed on Crist Unit 6 to replace SNCR. d.) WFGD means wet flue gas desulfurization (FGD) for sulfur dioxide (SO_2) control e.) SDA means spray dryer absorber for control. f.) DFGD means dry FGD for SO_2 control. g.) CFB means circulating fluidized bed. JEA Northside burns more petroleum coke than coal. h.) Limestone injection ($CaCO_3$) into the CFB bed for SO_2 control. i.) Polishing by lime (CaO) for SO_2 control. j.) Exhaust gases are scrubbed by cement kiln PM and filtered by cement kiln PM control device (a FF). k.) JEA SJRPP and TECO Big Bend process their fly ash through the collocated Separation Technology plants. IGCC means integrated gasification and combined cycle.				

*Data in this table was obtained from the NEED file provided by Alvaro Linero of FDEP.

5.2. Nationwide Trends in Air Pollution Control of NO_x

Comparing the current use of ammonia injection to control NO_x emission to nationwide trend, it is seen that Florida is ahead of the game, see Table 14. Currently, there are 15,021 power plant units in United States, among which, 1,514 units (10%) are equipped with SCR and 327 (2%) are equipped with SNCR for NO_x post-combustion control. For mercury control, activated carbon injection (ACI) technique is applied, but only in a small percentage of generating units (0.66%). Approximately 90% of the generating units operating an ACI system have reported efficiencies between 80% and 90%.

Table 14: SCR, SNCR and ACI in Power Plants of United States*

Technology	Equipment	No. of Units.	Percentage of all Generating Units
NO_x Post-Combustion Control	SCR	1514	10.08%
	SNCR	327	2.18%
Mercury Control	ACI	99	0.66%

*Data in this table was obtained from the NEED file provided by Alvaro Linero of FDEP.

5.3. Coal Fly Ash Processing Facilities

The only technology vendor (Separation Technologies, LLC) currently operating systems in Florida for ash conditioning to reduce ammonia in fly ash indicated that their typical practice is to limit ammonia concentrations to less than 75 ppm in fly ash. This vendor operates ash conditioning systems at two power plants in Florida.

As previously mentioned in Chapter 3: DOT Nationwide State Department Survey, the Missouri DOT determined that a maximum ammonia concentration in fly ash used in DOT project concrete mixes should be set at 100 ppm for the protection of workers from off-gassing ammonia. This view was echoed at other facilities that distribute fly ash, e.g. Tampa Electric Company. The limits proposed by industry facilities will be taken into consideration during this project's evaluation of ammonia limits in fly ash. It is important to consider the current practices of these facilities since it gives perspective on the current status of empirical knowledge of ammoniated fly ash use and feasibility of reducing ammonia concentrations in fly ash.

6. Preliminary Assessment of Potential Ammonia Release

The current use of ammonia injection at coal-fired units and regulatory limits for ammonia exposure for worker safety and environmental health were reviewed and summarized in the previous sections of this report. Additionally, representatives of the coal ash and cement industries in Florida were interviewed, and their current knowledge and experience with AFA was summarized. In this section of the report, information previously gathered was used to estimate the range of potential ammonia exposure to workers as a function of the amount of ammoniated fly ash used and its respective ammonia concentration.

6.1. Preliminary Assessment Objectives

The review and discussion in the previous sections of this report have demonstrated that elevated ammonia levels may occur in certain coal fly ashes and that those fly ashes might be used as a pozzolanic material in a concrete mixture. Before conducting experiments to determine the fate and behavior of ammonia in a concrete amended with ammoniated fly ash, it is beneficial to use a less intensive mass balance approach to simulate the "worst case scenario". If it is determined that ammonia would pose zero risk, using a conservative approach, additional testing may not be needed; however, if ammonia could possibly be problematic, it is pragmatic to pursue further knowledge through experimentation. The following section will illustrate such an approach.

However, it is not the intent of this preliminary assessment to provide site-specific conditions. Therefore, since many of the conditions that ultimately control contaminant transport and fate will not be site specific for this analysis, these conditions will be specified for a large range of values. For example, the dilution attenuation factor depends on the interaction of a multitude of site-specific factors. The dilution attenuation factor is defined as the ratio of contaminant concentration in soil leachate to the concentration in groundwater at the receptor point. As a result, it is impossible to predict dilution attenuation factors (DAF) without sufficient analysis of the site in question (EPA, 1993). However, a range of DAFs can be provided, and the result of their application can be observed.

6.2. Methodology

6.2.1. Potential Ammonia Releases to Soil and Water

As explained in Chapter 4, the public health and environmental risks associated with exposure to contaminants are used to determine minimum regulatory thresholds in soil, air, and water for those contaminants. It is important to keep this concept in mind throughout the mass balance assessment because the pathways of exposure and the fate of contaminants must be analyzed in unison.

To demonstrate the methods used in this mass balance, imagine a simple scenario where one ton of fly ash containing 3000 mg/kg total ammonia is applied to the land, with all of the ammonia present assumed to be $(NH_4)_2SO_4$. Referencing the SCTLs (soil pH = 5.04), one finds that for either residential (limit = 35,000 mg/kg) or commercial land use (limit = 860,000 mg/kg) the fly ash will not exceed the threshold. However, if the natural soil pH is not assumed and a more likely soil pH similar to that of fly ash (pH≥ 9) is assumed the SCTL is reduced to 1400 mg/kg for residential areas, see Table 11. For the purposes of this preliminary assessment, a soil pH of 9.5 will be assumed to model the "worst case scenario".

Next, the leaching of ammonium into the groundwater or surface water is assessed. Knowing that the solubility limit for ammonium sulfate in water is 740,000 mg/L, a simple calculation can be made to determine the minimum water required to dissolve all ammonium sulfate in the one ton of fly ash.

$$\frac{3000\ \mathrm{mgNH_3\ total}}{\mathrm{kg\ fly\ ash}} * \frac{\mathrm{kg}}{2.2\mathrm{lbs}} * \frac{2000\mathrm{lb}}{\mathrm{ton}} * 1\mathrm{ton\ fly\ ash} = 2700000\ \mathrm{mg\ or}\ 2700\ \mathrm{g\ NH_3\ total}$$

Then total ammonia is converted to ammonium sulfate (expressed as AS here).

$$2700\mathrm{g\ NH_3\ total} * \frac{\mathrm{mole\ NH_3}}{17\ \mathrm{g\ NH3}} * \frac{132\ \mathrm{g\ AS}}{\mathrm{mole\ AS}} * \frac{\mathrm{l\ water}}{740\ \mathrm{gAS}} = 28\ \mathrm{liters\ of\ water}$$

Therefore, it is seen that minimal water content is necessary for a large fraction of the ammonium to solubilize into interstitial waters of the substrate. If 28 liters of water dissolved all of the 2700 g of ammonia in the fly ash, and this contaminated solution directly discharged into a surface water body, or into groundwater recharge, the peak concentration could be around 96,400 mg/L. This, of course, is an unrealistic scenario; however, dilution attenuation factors can be applied to produce more realistic scenarios. This simple exercise demonstrates the methods with which one can analyze the behavior of ammonia in fly ash as it relates to regulatory limits.

In addition to the assumptions made earlier, it is now assumed that the cementitious materials content in the concrete is 752 lbs/ cubic yard, and that fly ash makes up the maximum 50% of the cementitious materials (FDOT, 2010). Using these assumptions one can arrive at a total mass of ammonia per cubic yard of concrete made.

$$\frac{3000\text{ mg NH3}}{\text{kg}} * \frac{\text{kg}}{2.2\text{ lbs}} * \frac{752\text{ lbs}}{\text{cubic yard}} = \frac{1000\text{ g NH3}}{\text{cubic yard}}$$

Assuming a concrete bulk density of 2400 kg/m^3 we have a total available ammonia concentration for concrete amended with AFA (3000 ppm) of 545 mg/kg. The total available ammonia for the fly ash (3000 mg/kg) and concrete (545 mg/kg) in this scenario will be used to illustrate potential releases. Additionally, if the same volume of leachate as was assumed for the fly ash (28L) is assumed here the maximum leachate concentration for the concrete would be 35,700 mg/L, assuming all ammonium solubilizes.

6.2.2. Potential Ammonia Exposure Due to Volatilization

Ammonia is released from mortar and concrete during mixing, placement, and curing. According to the University of Kentucky’s research, about 10% to 20% of the initial ammonia diffused from the concrete during 30 to 40 minutes of mixing, depending on the mix proportions and batch size. The following mass balance assessment of ammonia released into air will reference data in the UK’s research (Rathbone et al., 2003).

It is assumed that the concrete has an ammonia concentration of 545 ppm, 20% of which is released into the air during mixing. Ammonia gas is quickly and evenly distributed into the room. Additionally, the ammonia concentration in the air can vary with room size, ventilation rate and the amount of concrete poured at the site. In the following calculation, ACH (air changes per hour), the number of times the interior volume of air replaced per hour in an enclosed space, is used to represent different ventilation rates (ACH of 0, 0.1, 0.3 and 0.5 are used in the calculation). Additionally, the enclosed space is assumed to have a 50 m length, 50 m width, and 10 m height.

6.3. Preliminary Assessment Results

6.3.1. Potential Ammonia Release to Soil and Water

As can be seen in Figure 1 below, ammonia SCTLs vary with different soil pH values. If the total ammonia available in the fly ash sample and concrete specimen mentioned earlier is compared to ammonia SCTLs, it is apparent that it is unlikely that the concrete ammonia level will exceed the regulatory limits. However, at high soil pH values it is possible that the fly ash will exceed the regulatory limits.

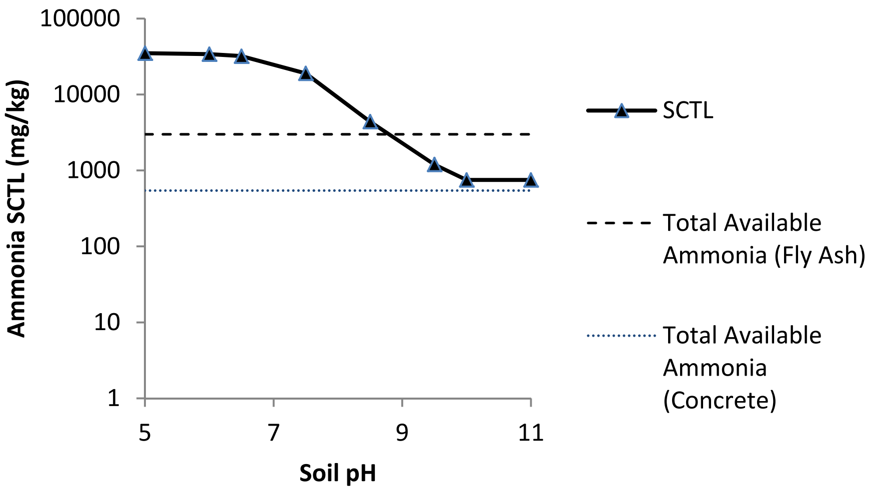

Figure 1: Ammonia SCTLs for Different Soil pH Values

Therefore, under most foreseeable exposure scenarios, the expected maximum ammonia level in concrete amended with AFA will not pose a significant danger to public health. However, the same cannot be said for the highly ammoniated fly ash itself. Indeed, there is anecdotal evidence to support this since most facilities that impound AFA onsite require workers operating in the impoundment area to wear respiratory personal protection equipment, i.e. respirators.

If the potential release to groundwater and surface water is considered, the graph in Figure 2 can be constructed which illustrates the potential release as a function of the DAF. As can be seen, if a very conservative estimate of the DAF is made, the ammonium concentration in the leachate from a soil amended with AFA or from a concrete specimen amended with AFA will exceed the regulatory limit. As a measure of typical DAFs, the EPA uses a DAF of 20 to calculate a leachability-based soil CTL for a contamination area with little known about site conditions and 0.5 acres in area. Therefore, with this assumed DAF in mind, the AFA alone and the AFA amended concrete specimen poses a potential risk to groundwater and surface water when viewed as a point source.

However, it should be noted that the concrete specimen was assumed to release all of its initial ammonium mass which is clearly an overestimate. At this time it is not clear to what extent either material, the AFA or concrete specimen, will release previously encapsulated ammonium to the environment. However, Figure 2 does show that the potential does exist that both materials could pose a risk to surface water and groundwater and more investigation is need to fully quantify these risks.

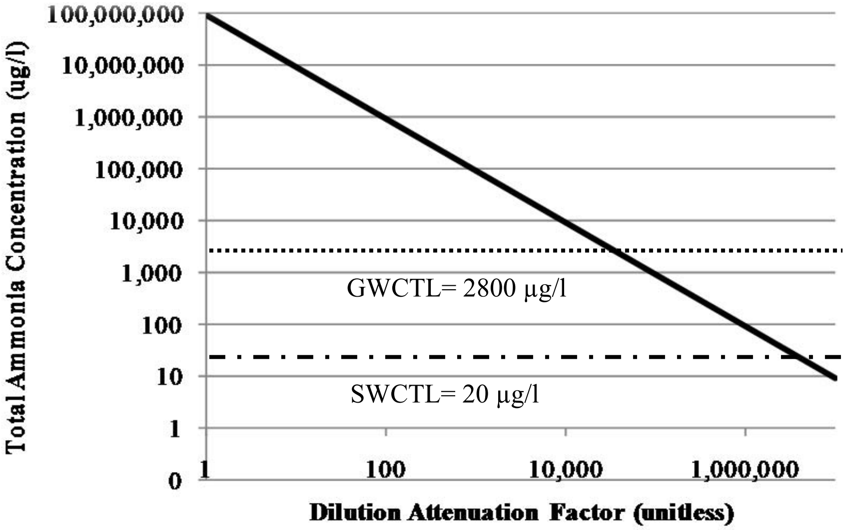

Figure 2: Total Ammonia Leaching from Fly Ash or Concrete with Dependency on Dilution Attenuation Factor

6.3.2. Preliminary Ammonia Volatilization Mass Balance Results

The relation between poured concrete amount and ammonia concentration in air is shown below in Figure 3. Also, the OSHA standard (50 ppm; 35 mg/m^3) and NIOSH standard (25 ppm; 17.5 mg/m^3) are pointed out in the figure. Larger concrete amounts poured at the site can cause possible worker exposure to ammonia concentrations higher than the regulation limit.

However, it is not taken for granted that the situation is more complex in reality. For example, after 30 to 40 minutes mixing, ammonia concentration in air usually decreases to a much lower level. In the following days and months, ammonia trapped in concrete slabs will further diffuse into the air. It should be noted that, according to UKY's research, ammonia concentration in the air did not exceed 25 ppm when the concentration in the concrete was less than 110 and 170 mg/L for non-ventilated and ventilated conditions, respectively.

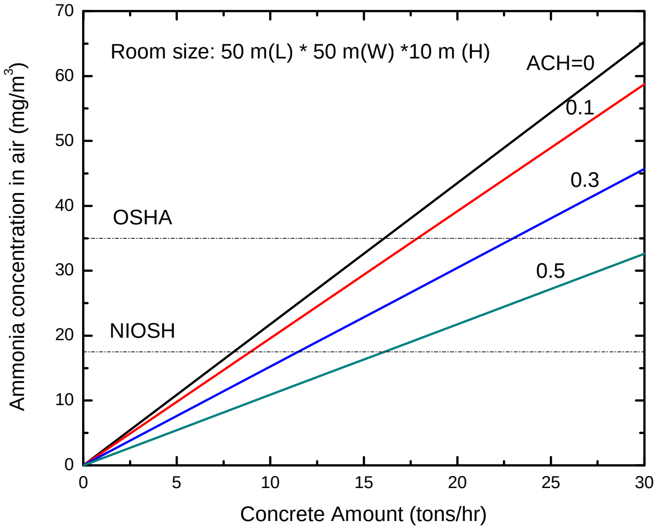

Figure 3: Ammonia Concentration as a Function of Concrete Deposition Rate

7. Experimental Methodology to Determine Mass Transfer Rates

The goal of the experimental methodology is to determine the mass transfer rates of ammonia/ammonium in concrete amended with Ammoniated Fly Ash (AFA) into various media, e.g. air, water, or leaching solution, and to use calculated mass transfer coefficients and diffusion coefficients to model other realistic scenarios.

7.1. Characterization of AFA

Fly ash samples originating from the Crystal River Power Complex were analyzed for ammonia content, loss-on-ignition (LOI) and moisture content as a preliminary characterization. A zero headspace vessel (ZHE) was used to make sequential extractions of a fly ash sample using deionized water at a LS ratio of 10:1. Each ZHE was mixed in an end-over-end fashion for one hour between extractions. The extraction fluid was analyzed by ion chromatography; the corresponding ammonium concentration of the extraction fluid can be used to directly measure the ammonium concentration absorbed onto the fly ash sample. It is assumed that all of the ammonium in the fly ash is of a form that is easily solubilized into water (Wang et al., 2002). The relationship between the ammonium concentration measured in the extraction fluid and the ammonium concentration absorbed onto the fly ash can be represented mathematically by the following expression.

$$C_{AFA} = C_{IC}\left[\frac{V_E}{m_{AFA}}\right] \quad (5)$$

Where C_{AFA} is the concentration of ammonium in fly ash (mg NH_3/kg AFA), C_{IC} is the measured concentration in extraction fluid (mg NH_3/L), V_E is the volume of extraction fluid used (L), and m_{AFA} is the mass of fly ash used (kg AFA). The fly ash was exposed to sequential extractions until ammonium concentrations in the extraction fluid are sufficiently low, generally less than one percent of the concentration in the first extraction (Wang et al., 2002). During each extraction 75% of the initial extraction fluid would be removed and analyzed for ammonium content. The fraction of extraction fluid removed for analysis would be replaced with new ammonium-free deionized water and the extraction and mixing process would be repeated. The cumulative concentration of ammonium in the extraction fluid can be calculated to determine the total ammonium content of the fly ash using the following expression

$$\mathrm{C_{AFA,Total}} = \mathrm{C_{IC,i}}\left[\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right] + \left[\mathrm{C_{IC,i+1}}\left(\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right) - \frac{\mathrm{C_{IC,i}}}{4}\right] + \left[\mathrm{C_{IC,i+2}}\left(\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right) - \frac{\mathrm{C_{IC,i+1}}}{4}\right] + \cdots \qquad (6)$$

The Loss-On-Ignition (LOI) of each fly ash collected was measured in accordance with ASTM D7348/ASTM C311. The fly ash was exposed to high temperature (750 ˚C) for an extended period of time (~4 hours) to burn off any remnant volatile solids, e.g. carbon content, water content, SO_3 content, or ammonium content, in the fly ash. Samples were weighed intermittently until a constant weight was attained. It should be noted that this measurement is not to be taken as a direct measurement of carbon content. Specifically, the method listed in ASTM D7348 warns against this inference. The moisture content was measured in a similar manner but at lower temperatures (105 ˚C) and for a longer time period (~24 hours) following ASTM C 311/ASTM D7348. The equation for determining LOI or moisture content can be seen in Equation 7 where m_i is initial mass of sample and m_f is final mass of sample.

$$\text{LOI or MC (\%)} = \frac{(\mathrm{m_i} - \mathrm{m_f})}{\mathrm{m_i}} \times 100 \qquad (7)$$

7.2. Sample Composition and Batch Schedule

For all tests in this experimental methodology the same concrete mix design was used. This was decided to isolate the variables that were considered the most important, i.e. concentration of ammonium in fly ash, cementitious content, fly ash replacement of cement, and water content (Rathbone et al., 2003). These variables were maximized to provide a scenario where the most ammonium would be present in a sample while still preserving possible mix ratios in accordance with FDOT specifications. As can be seen in Equation 8, increasing the cementitious content and fly ash replacement ratio will increase the concentration of ammonium in the intersitial water of the concrete mix thereby increasing the potential for ammonia release. The philosophy followed was that the “worst case scenario” was tested and more common scenarios can be predicted with some confidence that they will not exceed safety guidelines established in the extreme case.

In general, coarse and fine aggregates constitute 70-85% of concrete with the remaining 30-15 % consisting of water and cementitious materials (FDOT, 2010). While all concrete design mixes for FDOT construction projects must be pre-approved before their use, these specifications generally are concerned with mechanical properties of the concrete. For the purposes of the experiments in this report, it is not necessary to replicate an approved FDOT concrete mix design, since we are concerned primarily with chemical processes in the mix, i.e. ammonia concentration and volatilization. The parameters of most concern are the amount of cementitious material added to the mix, the percent of cementitious material replaced with fly ash, water content and the water to cementitious material ratio (Rathbone et al., 2003).

$$\mathrm{NH}_{4,\mathrm{water}} = \frac{[\mathrm{NH}_{4,\mathrm{ash}} \times \mathrm{CF} \times \mathrm{AR}]}{\mathrm{WF}} \tag{8}$$

Where, $NH_{4\ ash}$ is the concentration of ammonium in the fly ash (mg/kg), CF is the cement content of the concrete mix, AR is the fly ash replacement ratio, and WF is the water content. The fine and coarse aggregates remained constant in all batches, 30% and 40%, respectively. Also, the water to cementitious material ratio reflected the specifications set in the Standards for Specifications for Road and Bridge Construction Specifications Manual and remained constant and at the highest value for all classes of concrete approved by FDOT. The highest W/CM ratio was chosen due to the correlation observed between ammonia volatilization and high W/CM ratio (Rathbone et al., 2003). The amount of cementitious material added to our mix remained constant and at a level typically reserved for class V and VI concrete. This higher amount of cemetitious material was chosen to provide a scenario when the most fly ash would be present in a sample while still preserving mix ratios in accordance with FDOT specifications.

The gross composition of the concrete mix for the samples can be seen in Figure 4. The fly ash constituted 50% of the cementitious material with each fly ash having different ammonium concentrations, see Table 15 and 16 below. All samples were produced in duplicate and each sample was monitored for ammonia air emissions for one month or until the ammonia concentration was sufficiently low to be below detection limits. Additionally, leaching tests were used to determine the diffusion of bound ammonium in hardened concrete into an extraction fluid, e.g. deionized water.

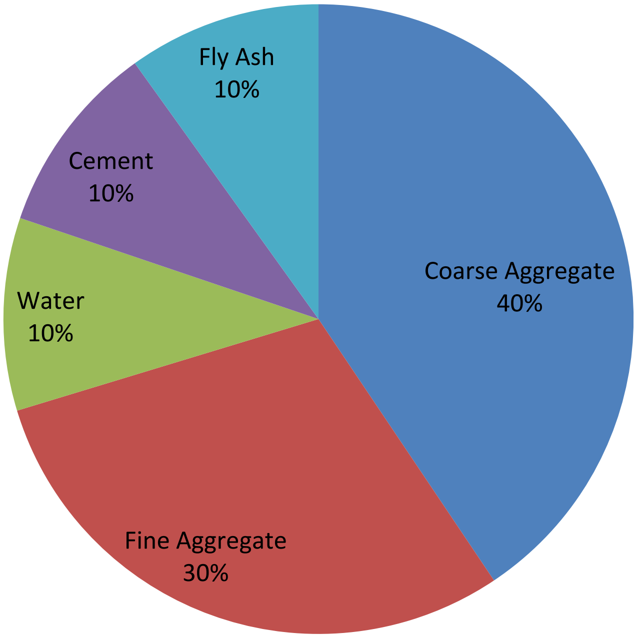

Figure 4: Gross Composition of Concrete Samples

Table 15: Composition of Concrete Batches for Experiments

Sample No.	Fly Ash Sample Used	*Cementitious Content per Cubic Meter of Concrete (kg)	Fly Ash Replacement Ratio (kg/kg cement)	Water to Cementitious Material Ratio (kg/kg)
Set 1	A	446.50	0.5	0.53
Set 2	B	446.50	0.5	0.53
Set 3	C	446.50	0.5	0.53
Set 4	D	446.50	0.5	0.53
Set 5	E	446.50	0.5	0.53
Blank	N/A	446.50	N/A	0.53

*Cementitious Content = Cement Content + Fly Ash Content

Table 16: Anticipated Ammonium Concentrations in Fly Ash

Sample ID	NH_4^+ Concentration in Fly Ash (ppm)
A	50
B*	500
C*	1000
D*	1500
E	3200

*Blended Fly Ash Concentrations of Fly Ashes A and E

Fly ash samples were collected from the Crystal River Power Complex in Crystal River, FL. Fly ash was collected from two coal combustion units at Crystal River Power Complex, Units 4 and 5. At the time received, i.e. 10/28/2011, unit 4 was producing a fly ash with significantly higher ammonia concentrations than unit 5, ~3200 and ~50 ppm (as reported by Crystal River Power Complex), respectively. Therefore, the two fly ashes were treated as separate materials; fly ash characterization can be seen in Table 21. An approximate total volume of 15 gallons of fly ash was collected and stored in air-tight glass or HDPE bottles. It was decided to blend the two fly ash samples, in varying amounts, to produce fly ash blends with different ammonium concentrations than the original samples. The anticipated ammonium concentrations of fly ash samples can be seen in Table 16.

Portland cement (Quikrete® ASTM C150-Type I) was purchased for use in all concrete mixes. Coarse (Quikrete® ASTM C33, 1/4", maximum nominal diameter) and fine aggregates (Quikrete® ASTM C33) were purchased for concrete mixes in ammonia volatilization experiments. The coarse and fine aggregates for the monolith leaching tests were received from the FDOT State Materials Lab, Gainesville, FL. The smaller stone aggregate was necessary for the volatilization concrete mix due to its smaller volume and dimensions. All aggregate parameters can be seen in Tables 17 and 18. Fine aggregate consisted of siliceous sand graded to ASTM C33 specification. Coarse aggregate consisted of limestone graded to ASTM C33 specification; coarse aggregate was saturated, surface dry upon use in concrete mixes.

Table 17: Coarse Aggregate Characterization

Coarse Aggregate	Maximum Nominal Diameter (inches)	Absorbance (%)
Quikrete® ASTM C33	0.25	6.5
FDOT ASTM C33	0.5	3.5

Table 18: Fine Aggregate Characterization

Fine Aggregate	Fineness Modulus	Moisture Content (%)
Quikrete® ASTM C33	2.61	0.15
FDOT ASTM C33	2.25	0.2

7.3. Semi-Infinite Model of Diffusion

Calculation of the interface diffusion coefficient between the concrete and air is based on the semi-infinite diffusion model (Glicksman, 2000) which is applied to a diffusion process from a source (e.g., a cylinder, a plate or a slab) to infinite bath. The situation of ammonia releasing from concrete slab into atmosphere or leaching into water can both apply to this model. A simple deduction process is shown as below:

A typical concentration-distance curve for an ongoing time-dependent diffusion process can be described by Equation (9):

$$C(x,t) = C_0 e^{-\frac{x}{\lambda}} e^{-\frac{t}{\tau}} \tag{9}$$

where its second derivative is:

$$\frac{\partial^2 C(x,t)}{\partial x^2} = \frac{1}{\lambda^2} C_0 e^{-\frac{x}{\lambda}} \cdot e^{-\frac{t}{\tau}} \tag{10}$$

Fick's 2nd law describes the concentration change with respect to time and location,

$$\frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{11}$$

Replacing the concentration divergent in Equation (11) with Equation (10), the concentration change with respect to time can be obtained:

$$\frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) = \frac{D}{\lambda^2} C_0 e^{-\frac{x}{\lambda}} \cdot e^{-\frac{t}{\tau}} \tag{12}$$

According to semi-infinite diffusion model, initial and boundary conditions can be written as:

1) Fixed surface concentration, $C(0, t)=C_0$;
2) Initial concentration outside the source equals to 0, $C(x, 0)=0$;

With these two conditions applied to Equation (12), solutions of the semi-infinite model can be obtained as Equation (13) (Glicksman, 2000):

$$C(x,t) = C_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right) \tag{13}$$

where,

$$erfc(z) = 1 - erf(z) = 1 - \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-u^2} du \qquad (14)$$

To obtain a solution for the mass release rate, get first derivative of Equation (13) with respect to distance and multiply diffusion coefficient D on both sides:

$$\left(D \frac{\partial C}{\partial x} \right)_{x=0} = \frac{DC_0}{\sqrt{\pi Dt}} \qquad (15)$$

Integrating both sides with respect to time t, Equation (15) can be written as:

$$\int_0^t D \frac{\partial C}{\partial x} dt = \int_0^t \frac{DC_0}{\sqrt{\pi Dt}} dt \qquad (16)$$

Note D on both sides can be canceled out.

Then, according to Fick's first law,

$$J = -D \frac{\partial C}{\partial x} = -\sqrt{\frac{D}{\pi t}} C_0 \qquad (17)$$

where J is diffusion flux. So Equation (16) can be transformed to:

$$\int_0^t \frac{J}{-D} dt = \int_0^t \frac{C_0}{\sqrt{\pi Dt}} dt \qquad (18)$$

This reveals the following relationship:

$$M_t = \int_0^t J dt = 2C_0 \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}} \qquad (19)$$

Where M_t is cumulative mass release per area, (mg/m^2)

So, at a time interval Δt, we have:

$$D_i = \frac{\pi}{\Delta t}\left[\frac{\Delta M_t}{2C_0}\right]^2 \tag{20}$$

Based on experimental measurements of mass released over time, Equation 20 can be used to calculate the diffusion coefficient as a function of time. This model was used to calculate the diffusivity of ammonia/ammonium into air or water from a concrete matrix.

7.4. Ammonia Release during Mixing and Curing

To assess ammonia release during the mixing and curing of concrete made with AFA, the concrete mixing process was simulated in an enclosed chamber. The chamber, as seen in Figure 5, is equipped with multiple ports for gas exchange and gloves to allow access. Herein this chamber is referred to as a “glove box”. The experimental protocol had the following three steps: 1) mixing of batch components; 2) pouring of wet concrete into mold; and 3) initial curing stage. The mixing period lasted 3 minutes. Compositions and proportions of each component are listed in Table 19. Proportions of each component were decided according to the specification in Table 15. Five different concrete sample sets, as shown in Table 15, were tested. After the concrete was completely mixed, it was poured into a mold (10.5”x 2.5”x 2.5”) and allowed to stay in the mold for initial setting. The glove box experiment lasted 8 hours. It usually took 7 to 8 hours for a concrete slab to be hardened in the glove box. Ammonia concentration in the glove box also needed certain time to decrease to lower than 50 ppm (OSHA standard) by ventilation.

Table 19: Concrete Composition and Weight of Concrete Samples in the Glove Box Experiment

Concrete Composition	**Weight (g)**
Coarse Aggregate	550 g
Fine Aggregate	375 g
Cement	188 g
Water	199 g
AFA	188 g
Total	**1.5 kg**

After the expected peak level of ammonia had passed and the concrete sample had sufficiently set; the sample was moved to a closed container to cure and monitored for ammonia release for an extended period. The critical time that samples remained in the glove box was initially set at 16 hours; this time was based on observations from Rathbone and Robl, 2001. However, our observations differed from that paper; the sampling time was therefore adjusted as deemed necessary, i.e. 8 hours. The experimental setup for the glove box (Phase I) and the curing boxes (Phase II) can be seen in Figures 5 and 6.

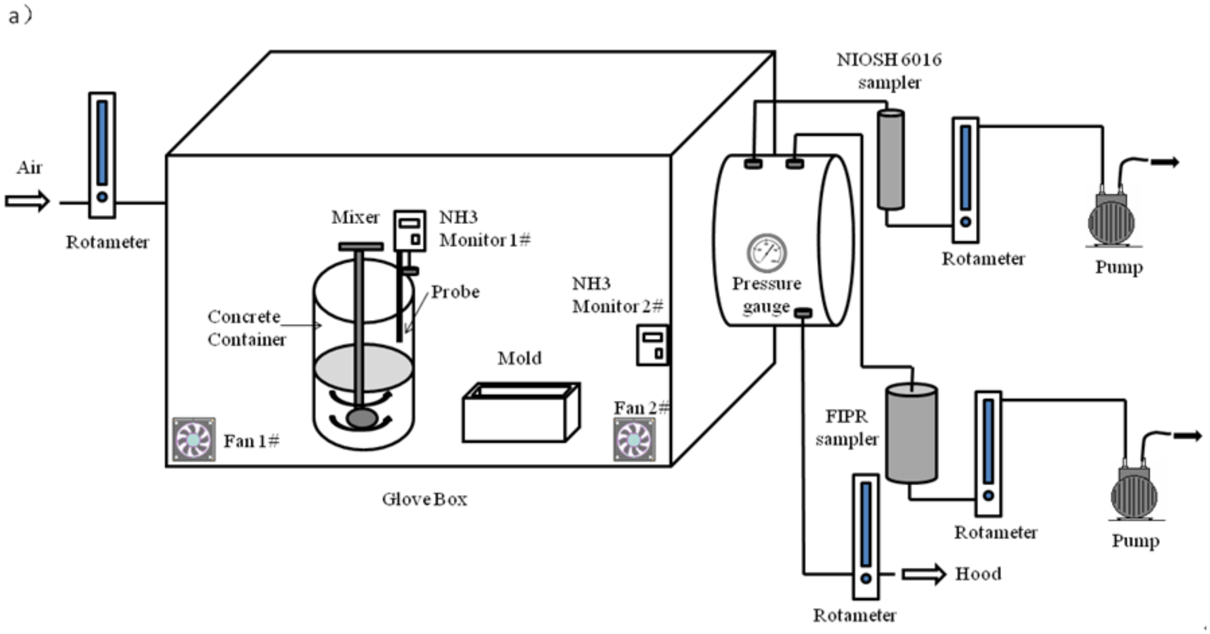

Figure 5: Experimental Setup of the Glove Box: a) schematic; b) photo

Inside the glove box, there were two fans installed at both sides of the glove box to create enough turbulent flow to ensure that released ammonia was evenly distributed throughout the glove box. Two real-time ammonia gas monitors measured ammonia concentration in the air contained in the glove box: one probe was positioned above the surface of concrete to measure the concentration near the concrete interface; another monitor was placed at a corner of the glove box to measure the ambient ammonia concentration in the chamber. A silica gel absorbent sampling tube, used in accordance with NIOSH Method 6016, and a FIPR sampler were connected with a rotameter and a pump to continuously collect gas from the glove box. The flowrate of the FIPR personal sampler was set to be 2±0.2 L/min, while that of the NIOSH sampler was 0.5±0.05 L/min. In order to maintain ambient pressure in the glove box, clean air was sent to the glove box with a flowrate of 2.8±0.1 L/min. A fourth line connected to the hood was used to ensure pressure balance in the glove box. A full description of these sampling devices can be found in Appendix II. The NIOSH 6016 sampler and the denuder in the FIPR sampler were changed in a certain time interval. After sampling, the samples were extracted using DI water. The extracted NH_4^+ concentration was then analyzed by an Ion Chromatography (IC) system for time-weighted average (TWA) values. The results from the two sampling systems were compared with that from the real-time monitor and were used to calculate the interface diffusion coefficient.

After 8-hours, the concrete slab was removed from the glove box and placed in a sealed container. This allowed the monitoring of ammonia release during curing. The experimental setup of this phase is shown in Figure 6. A controlled air flowrate (1.5±0.2 L/min) of ammonia-free air was used and ammonia gas was allowed to diffuse into the carrier gas. The container was connected to an impinger with a 0.1 N H_2SO_4 solution to collect ammonia gas diffused into the carrier gas. The solution in the impinger was analyzed by IC and replaced daily.

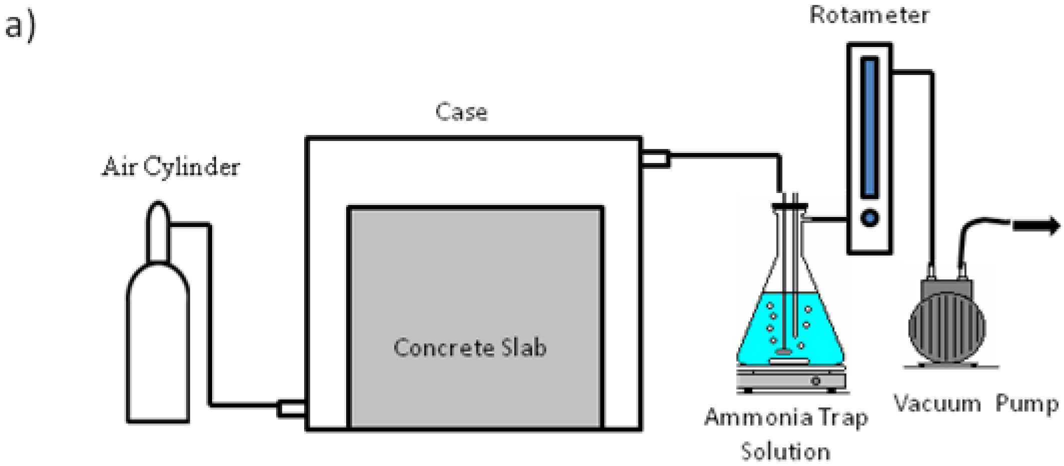

Figure 6: Experimental Setup of the Curing Boxes: a) schematic; b) photo

7.4.1. Released Ammonia Percent (RAP) and Cumulative Mass Release (M_t) Calculation

The overall ammonia gas volume leaving the concrete slab can be calculated as follows:

$$V_{NH_3} = \sum_{i=0}^{t} C_i \cdot \dot{Q}_i \cdot \Delta t + V_G \cdot C_t \tag{21}$$

where,

V_{NH_3} : overall ammonia gas volume, L;

C_i : glove box ambient ammonia concentration at time *i,* ppm (V/V);

$\dot{Q}_i$: air flow rate at time *i,* L/min;

Δt : time interval, min

t: overall glove box experiment time, min;

V_G : glove box size, 470 L;

C_t : ambient ammonia concentration at the end of the experiment, ppm (V/V).

The overall ammonia gas volume, V_{NH3}, can then be converted to overall ammonia mass by the ideal gas law:

$$P \cdot V_{NH_3} = \frac{M_{NH_3}}{MW_{NH_3}} \cdot R \cdot T \tag{22}$$

where,

P: ambient pressure in the glove box, 1 atm;

MW_{NH_3} : ammonia molecular weight , 17.03 g/mol;

R: universal gas law constant, 0.082 (atm)(L)/(g mole)(°K);

T: ambient temperature of the glove box.

The released ammonia percentage (*RAP)* can be calculated as:

$$RAP = \frac{M_{NH_3}}{M_{AFA} \cdot C_{AFA}} \tag{23}$$

M_{AFA}: mass of AFA used in the experiment; g.

C_{AFA} : ammonia concentration of the AFA used in the experiment; ppm (M/M).

Cumulative mass release M_t in the semi-infinite diffusion model can be obtained by:

$$M_t = \frac{M_{NH_3}}{A_{\text{int}erface}} \tag{24}$$

where $A_{\text{int}erface}$ is the interface surface area between the concrete slab and air; cm^2

7.4.2. Mass Transfer Coefficient Calculation

Mass transfer coefficient (k) can be calculated in the following equation:

$$k = \frac{J}{C_i - C_i'} \tag{25}$$

Where J is the flux at the interface; C_i and C_i' are the concentrations at the interface and in the bulk solution, respectively (Cussler, 1991).

In a time period from 0 to t_0,

$$\overline{J} = \frac{\int_0^{t_0} \sqrt{D/\pi t}\,\Delta C dt}{t_0} = 2\sqrt{D/\pi t_0}\,\Delta C \tag{26}$$

Thus,

$$\overline{k} = 2\sqrt{D/\pi t_0} \tag{27}$$

7.5. Leaching Tests

Leaching tests were conducted on the hardened concrete samples to determine mass transfer rate and total leachable ammonium from the concrete matrix. These tests included the Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312) and the Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test (EPA Draft Method 1315). Concrete mix designs for samples for both leaching tests were identical. The mix design proportioning can be seen in Table 15. However, only three of the sample sets were mixed, i.e. Set 1, 4 and 5, with the addition of a blank sample containing no fly ash. Initial ammonia concentration varied between sets; however, all other variables, i.e. coarse and fine aggregate content, cement content, fly ash content (with the exception of the blank) and water content, were identical for all sets. Constituent concentrations can be seen in Table 20 below.

7.5.1. Synthetic Precipitation Leaching Procedure (EPA Method 1312)

Concrete samples were mixed and placed in cylindrical molds; samples and molds were wrapped in plastic sheeting to ensure a high humidity environment for the initial 48 hour curing period. After samples had been cured for 48 hours, they were removed from the molds and size reduced in a jaw crusher to a diameter less than 1 cm. Samples were then ready for extraction by EPA Method 1312: Synthetic Precipitation Leaching Procedure.

The Synthetic Precipitation Leaching Procedure (SPLP) is an EPA SW-846 method for determining the mobility of contaminants in a liquid, soil, or waste under weathering conditions. For solid phase waste, e.g. fly ash or concrete, the waste is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is deionized water, and the solid phase and solution were sealed and mixed in an end-over-end fashion for approximately 18 hours. Following extraction, the liquid extract was separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. This liquid extract was then stored at pH 2 for later analysis with an ion chromatograph. The SPLP was used as a measure of total leachable ammonium from the hardened concrete samples.

7.5.2. Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test (Method 1315)

Concrete samples were mixed and placed in cylindrical molds; samples and molds were wrapped in plastic sheeting to ensure a high humidity environment for the initial 48-hour curing period. After the concrete samples had been cured for 48 hours, they were removed from the molds and were anchored to the lid of a Gamma Seal® bucket as can be seen in Figure 7. Gamma Seals® are air-tight container lids that can be placed on many 3.5 – 7 gallon HDPE buckets. Samples were than ready for extraction by EPA Draft Method 1315: Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test.

Figure 7: Monolith Suspended from the Lid of Gamma Seal® by Nylon Cord

EPA Draft Method 1315 is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic or compacted granular material, under diffusion-controlled release conditions, as a function of leaching time. The method comprises leaching of continuously water-saturated monolithic or compacted granular material in an eluent-filled tank with periodic renewal of the leaching solution, refer to Figure 8. Samples are contacted with deionized water at a specified Liquid to Surface Area (LSa) ratio. The leaching solution is exchanged with fresh ammonium-free water at nine pre-determined intervals (USEPA, 2009). As can be seen in Figure 7, all faces of the monolith were exposed to the leaching solution and care was taken to minimize headspace and to create an air-tight seal to reduce any fugitive ammonia release into the vessel headspace or outside of the vessel.

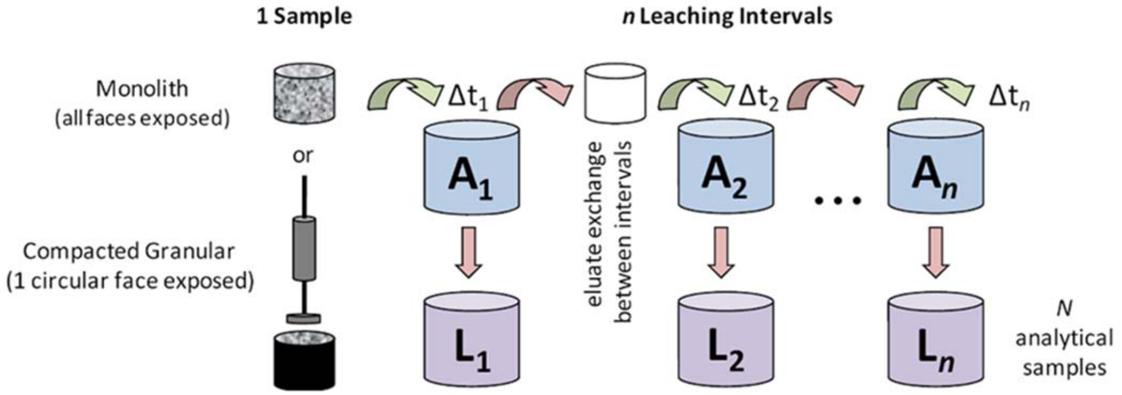

Figure 8: Schematic of Monolithic Leaching Procedure Leaching Intervals

Note: Reprinted from “EPA Draft Method 1315” by United States Environmental Protection Agency, 2009.

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Table 20: Concrete Mix Design Proportions for Monolith Used in Leaching Tests

Concrete Mix Constituent	Mass Used (kg)
Fly Ash Content	0.716
Water Content	0.759
Cement Content	0.716
Coarse Aggregate Content	2.892
Fine Aggregate Content	2.170

7.5.3. Application of the Semi-Infinite Diffusion Model to Semi-Dynamic Tank Leaching

Based on the data collected from Method 1315 (cumulative mass release rates of ammonium), a semi-infinite medium diffusion model was used to calculate the observed diffusivity of ammonium in the concrete matrix of the hardened concrete samples. A complete derivation of this model can be seen in Section 7.3: Semi-Infinite Model of Diffusion. Assuming the semi-infinite medium diffusion model, it is appropriate to visualize the concrete monolith as a cylinder diffusing radially into an infinite bath of deionized water. The diffusion coefficient for ammonium can be used to predict release rates of ammonium in hardened concrete under different scenarios, e.g. concrete of different dimensions and ammonium concentrations (Kosson et al., 2009; Torras et al., 2011). It should be noted that this model is based on the same initial and boundary conditions as the semi-infinite diffusion model used to develop the ammonia diffusion coefficient into air. However, the data collected from measurements and the diffusion medium is different and explanation of the model with emphasis to its use in determining leaching mechanisms and rates is warranted.

Leaching can be affected by a number of factors, including pH, temperature, chemical and physical encapsulation of analytes, and leaching solution chemistry. However, with respect to leaching of analytes from monoliths, three main mechanisms which generally control the leaching process are surface wash off, diffusion transport, and surface dissolution (Torras et al., 2011). Surface wash off is a process by which the surface concentration of the analyte on the monolith is quickly solubilized into the bulk leaching solution. Diffusion transport is the migration of analytes by random motion from higher to lower concentration through a medium, i.e. concrete. Surface dissolution is the physical solubilization of the medium into the leaching solution. Utilizing a semi-dynamic monolith leaching test, e.g. Method 1315, allows one to determine the main leaching mechanism, mass transfer rate, and changes in the leaching mechanism over time (Torras et al., 2011).

If the diffusion controlled leaching mechanism is assumed, a predictive model of ammonium diffusivity in a hardened concrete matrix can be constructed. That is, using the simple radial diffusion from a cylinder into an infinite bath model and the results from the semi-dynamic leaching test one can calculate the effective diffusivity of ammonium in hardened concrete and thereby predict mass release rates in other concrete monolith geometries and concentrations of ammonium (Kosson et al., 2009). If the medium (deionized water) that the analyte (ammonium) is diffusing into is of sufficient volume then the simple radial diffusion from a cylinder into an infinite bath model has been suggested as a predictive model (Kosson et al., 2009).

Use of a simple radial diffusion from a cylinder into an infinite bath model is prefaced on the following assumptions: (a) analyte, i.e. ammonium, depletion within the monolith does not occur, (b) the diffusion coefficient of the analyte is constant, and (c) the concentration of the analyte within the leaching solution remains low compared to the source concentration, such that the concentration gradient driving the analyte diffusion remains sufficiently high. While this model does have limitation, as noted by the assumptions above, the model used in conjunction with the semi-dynamic leaching test is practical and predictive (Kosson et al., 2009; Torras et al., 2011).

An analytical solution of Fick's Second Law can be formulated using the following initial and boundary conditions: (a) the surface concentration of the monolith is assumed to be constant, (b) the concentration of the ammonium is uniform throughout the monolith and known initially and (c) the final concentration within the monolith is not zero. If these initial and boundary conditions are assumed, the solution to Equation 10 can be written in the form as that in Section 7.3. An analytical solution to Equation 10 is provided below in Equation 28:

$$\frac{C(x,t)-C_s}{C_i-C_s} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{28}$$

Where, C(x, t) is the concentration within the monolith with respect to position and time, C_i is the initial uniform ammonium concentration, C_s is the surface concentration, erf is the error function, x is the depth into the monolith, D is the diffusion coefficient, and t is time. Assuming a uniform initial ammonium concentration is equal to the constant surface concentration and depletion does not occur; the mass loss rate per unit area (mg/m^2) can be calculated by Equation 9 in Section 7.3.

Alternatively, the mass loss per unit area can be calculated from experimental data using the relationship seen in Equation 29.The observed diffusion coefficient is the measurement of diffusivity calculated from data of the semi-dynamic leaching test (Method 1315). The observed diffusion coefficient can be calculated using the relationship seen in Equation 12 in Section 7.3, an alternative form of Equation 12 is provided below in Equation 30.

$$M_{t_i} = \frac{C_{meas} V_i}{A} \tag{29}$$

Where, C_{meas} is the concentration of analyte measured in the leaching solution after the leaching interval, V_i is the volume of leaching solution used, and A is the surface area of the monolith exposed to the leaching fluid.

$$D^{obs} = \pi \left[\frac{C_{meas} V_i}{2 \rho A C_i \left(\sqrt{(t_i - t_{i-1})} \right)} \right]^2 \tag{30}$$

Where, $\sqrt{t_i}$ is the cumulative leaching time for the current leaching interval, $\sqrt{t_{i-1}}$ is the cumulative leaching time for the previous leaching interval, and ρ is the measured density of the monolith. Additionally, the analyte flux (mg/m^2-s) can be calculated from experimental data. The relationship observed in Equation 31 can be used to calculate the analyte flux.

$$J_i = \frac{M_{t_i}}{t_i - t_{i-1}} \tag{31}$$

8. Experimental Results

8.1. Fly Ash Characterization

As can be seen in Figure 9, the majority of ammonia (>95%) is extracted during the first extraction of fly ash Sample E. This trend was observed for all other fly ashes as well, i.e. Samples A - D. These results mirror those found by Wang et al. in a 2002 study using a similar extraction method. Therefore, only two extractions were conducted on fly ash samples. The observed concentrations for all fly ash samples can be seen in Table 21.

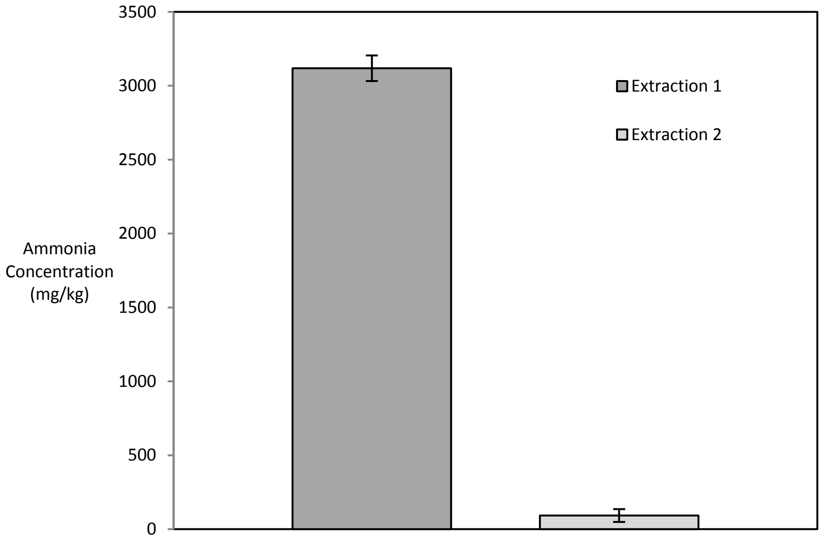

Figure 9: Ammonium Extraction of Fly Ash Samples

The ammonium concentrations were all measured using the extraction procedure outlined in Section 7.1: Characterization of Fly Ash. The loss-on-ignition measurements for all fly ash samples were consistent. It is noted that the LOI measurement is higher than the specification for the use of fly ash in ASTM C311; however, the fly ash used in experiments and subsequent concrete mixes were collected before any beneficiation practices were utilized to produce a more marketable fly ash. As such, the fly ash was used as received.

Table 21: Fly Ash Characterization Results

Sample Identification	Measured NH_4^+ Concentration (ppm)	Loss-On-Ignition (%)	Moisture Content (%)
A	65	11.2	0.21
B*	500	11.2	0.15
C*	862	11.2	0.10
D*	1378	11.2	0.22
E	3211	11.2	0.22

*Fly ash was blended from samples A and E to create desired ammonium concentrations

8.2. Ammonia Volatilization

8.2.1. Glove Box Experiment

Ammonia gas concentration trends for mixing concrete Sets 1 to 4 in the glove box are shown in Figures 10 a) to d), respectively. As shown, ammonia concentration at the surface of the concrete was always higher than that of the ambient, which shows that the concrete was continuously releasing ammonia during the 8-hour glove box experiment. Due to a high diffusion coefficient in air and adequate turbulent flow created by the two fans in the glove box, ammonia released from the concrete interface was distributed quickly to the entire glove box. In Figure 10a), for concrete Set 1, the peak concentration detected by the real-time monitor, NIOSH sampler and personal sampler were 5.4 ppm, 6.5 ppm and 5.9 ppm, respectively. The overall tendencies of the three ammonia sampling systems were similar during the experiment. For the concrete with higher ammonia content, the peak concentration of ammonia in the air increased accordingly, as shown in Figures 10b) – 10d). The capacity of the NIOSH 6016 sampler and the FIPR personal sampler was shown to be insufficient under these conditions. The FIPR personal sampler is still in development by Dr. Wu's group, while the standard NIOSH 6016 method shows a smaller capacity than referenced in the NIOSH methodology (NIOSH, 1996; NIOSH, 1977). In the NIOSH method, the maximum volume of the NIOSH 6016 sampler is 96 L at 50 ppm, which means 3.3 mg of NH_3 can be absorbed. However, in Figure 11b), the highest amount of ammonia absorbed was 0.63 mg (30 L at 30.5 ppm), only 19% of the reported capacity. In

Figure 11d), under higher ambient ammonia concentration (peak at 200 ppm), the highest capacity of the NIOSH 6016 sampler was 1.7 mg (30 L at 82 ppm), about 50% of the reported capacity. Therefore, it is recommended that the capacity of the NIOSH 6016 sampler and its working conditions be reviewed again.

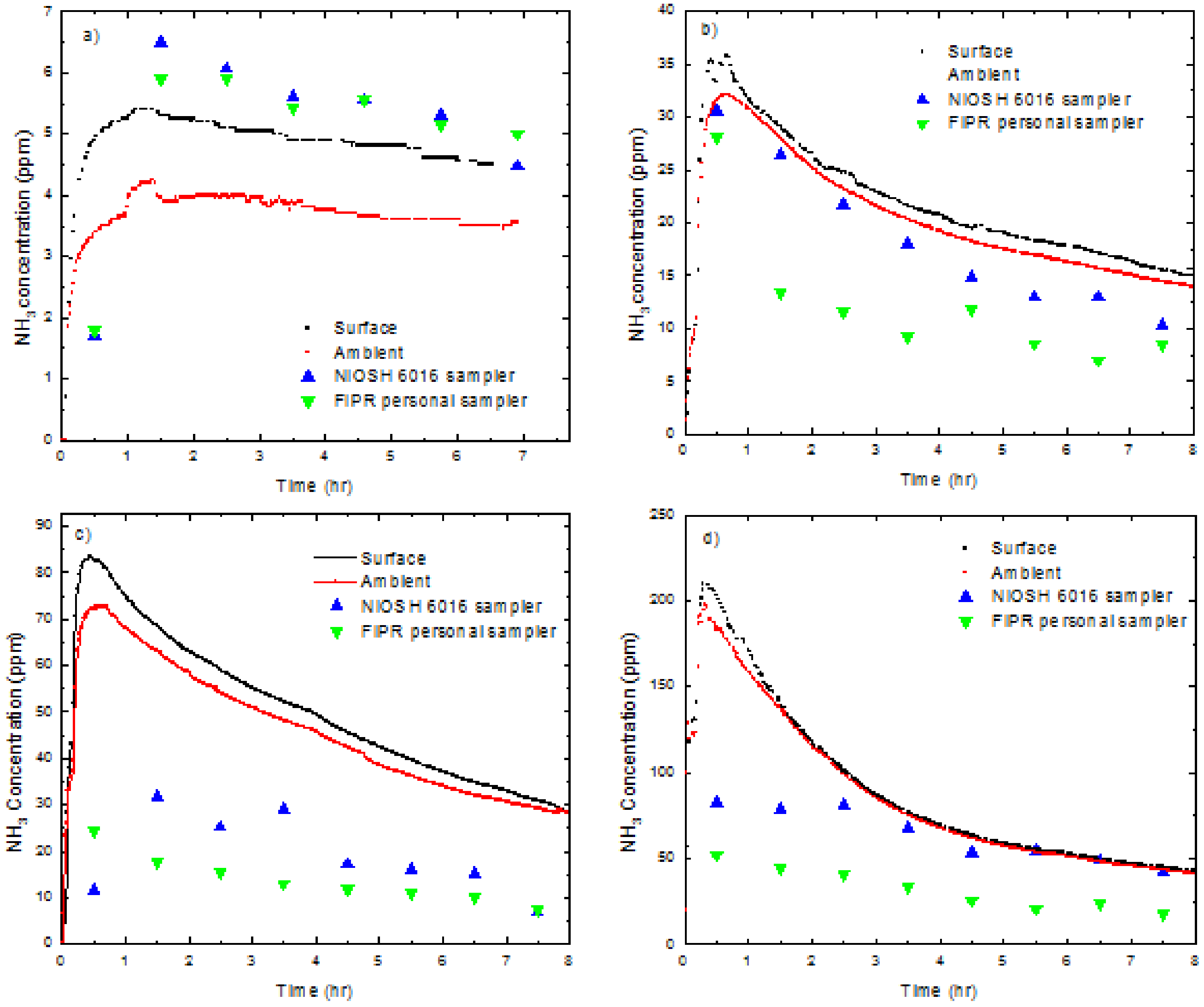

Figure 10: Measured Ammonia Emissions from Concrete Specimen: a) Set 1; b) Set 2; c) Set 3; d) Set 4

The ammonia concentrations in the glove box measured by the real-time monitors throughout the course of the experiment for all concrete specimens are summarized in Figure 11. As shown, in all five sets of concrete specimens, the peak concentration of ammonia was observed approximately 20 minutes after the experiment started.

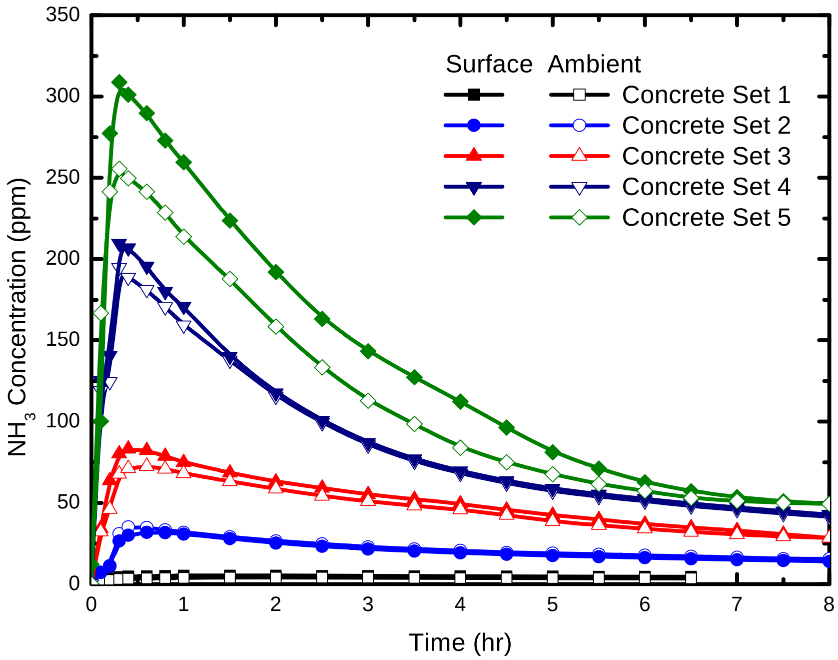

Figure 11: Real-Time Monitor Measurements of Ammonia Concentration during Mixing and Initial Setting of Concrete Specimens

The cumulative ammonia released by mass of the five groups of experiments was calculated and is presented in Figure 12. According to Equation 19 in Section 7.3, it is clear that if ammonia release follows the semi-infinite model, then cumulative mass release should by proportional to $\sqrt{t}$ if the diffusion coefficient is constant. The relationship between M_t and $\sqrt{t}$ can be written as:

$$M_t = K\sqrt{t} \tag{32}$$

where

$$K = \frac{2C_0\sqrt{D}}{\pi} \tag{33}$$

So the diffusion coefficient can be calculated as

$$D = \left(\frac{K\pi}{2C_0}\right)^2 \tag{34}$$

This relationship is shown in Figure 12, which indeed shows a linear relationship between cumulative mass release and $\sqrt{t}$. However, in all samples, the slope changed after 25 minutes. The possible reason may be related to the process of mixing of concrete during the glove box experiment. In the first 10 minutes, water was poured into the concrete, and the concrete was continuously mixed for a predetermined interval before the mix was poured into a mold. During this process, outside work was introduced to the concrete mix system, and the cement was undergoing an exothermic reaction, which enhanced ammonia release to some extent. After the concrete was placed in the mold and during the concrete setting, there was no more outside work being done to the system. The ammonia release was largely due to the concentration gradient and high pH of the concrete. Therefore, the diffusion coefficient during the mixing period is greater than during the setting of the concrete. The slope change of the two periods, as shown in Figure 12, also verifies this possibility. Therefore, in order to calculate the diffusion coefficients of the two periods, the relationship between M_t and $\sqrt{t}$ was separated into two intervals, as shown in Figure 13 a) and b). The diffusion coefficients were calculated according to the value of K as shown in Table 22 and Figure 14. As shown, the diffusion coefficients during the first period (D_1) was not necessarily related to initial ammonia concentration in AFAs, while that of the second period (D_2) decreased as ammonia concentration in AFA increased. This tendency is probably related to overall released ammonia percentage (RAP) of each type of AFA, as shown in Figure 15. For a concrete slab of the same mass and shape, the higher ammonium content it contains, the lower fraction of ammonia will be released into air.

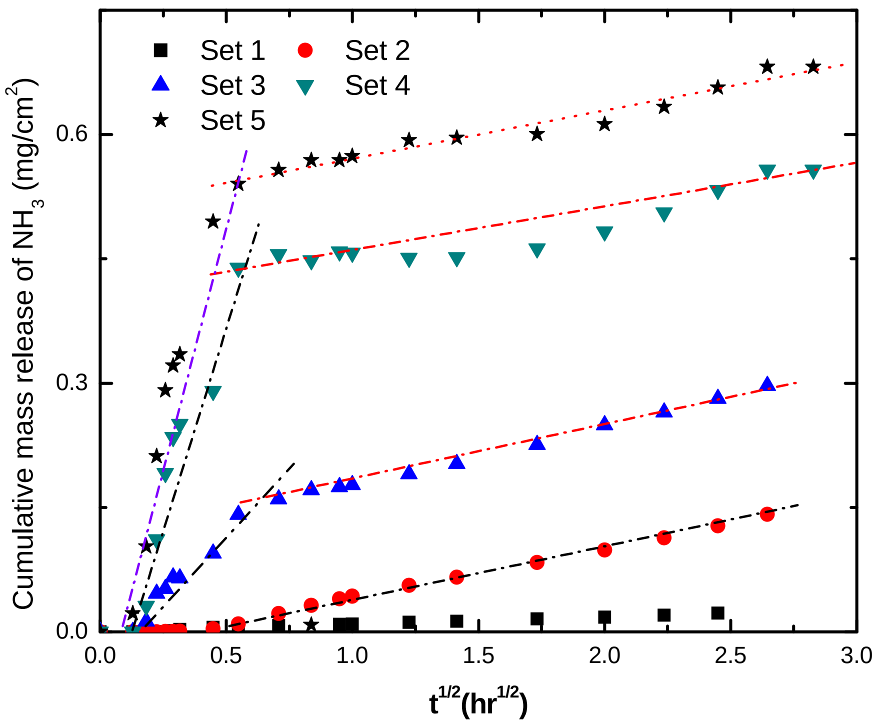

Figure 12: Cumulative Mass Release of Ammonia as a Function of $\sqrt{t}$

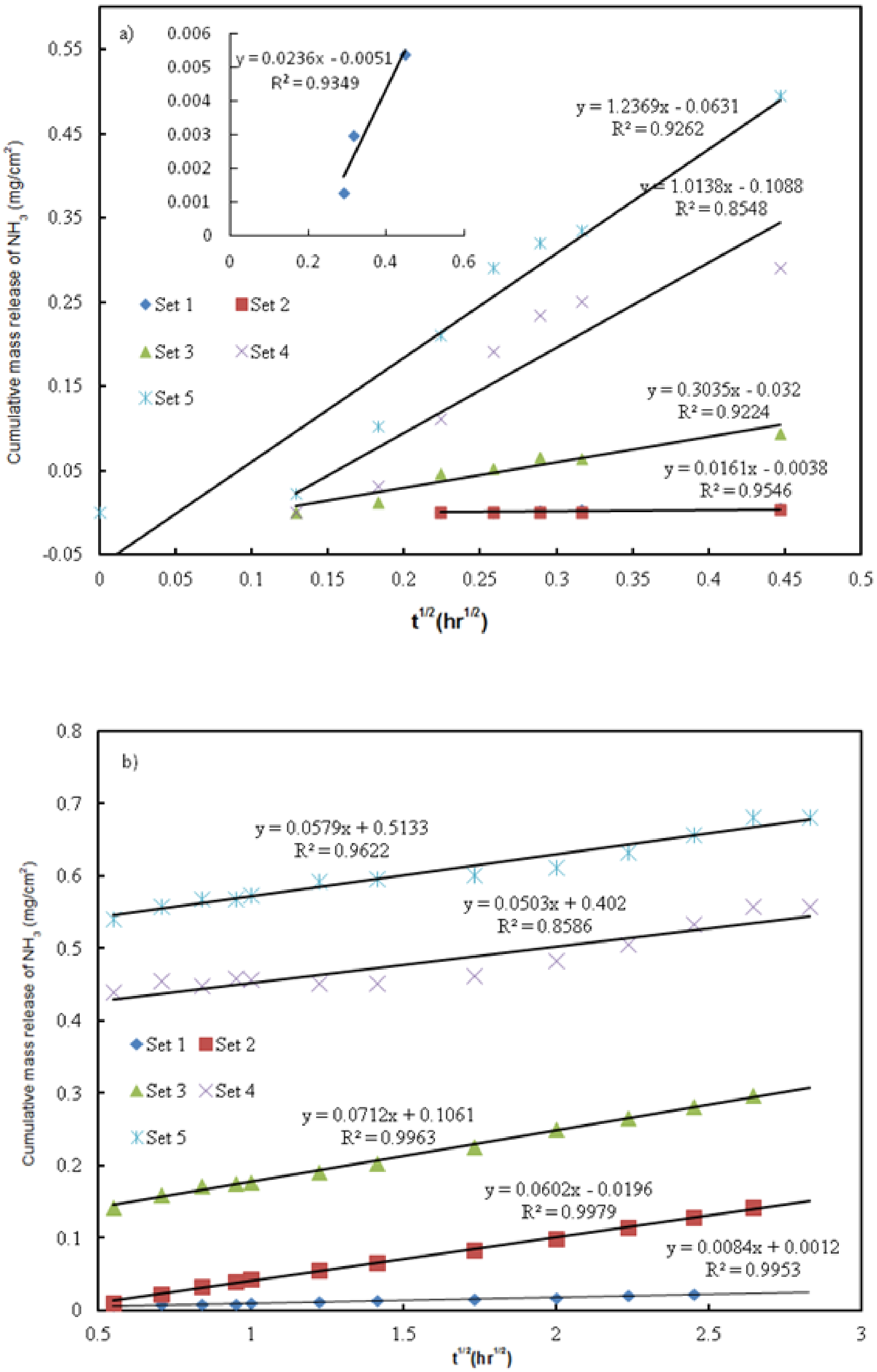

Figure 13: Linear fitting of M_t vs. $\sqrt{t}$: a) the first 25-min period; b) the second 25th min-8th hour period

Table 22: Diffusion Coefficients of the First and Second Period for the 5 Sets of Concrete in the First 8-Hour Mixing and Curing Period

Set	Initial ammonia concentration C_0		First Period			Second Period		
	ppm	mg/cm^3	K_1	R_1^2	D_1 (cm^2/s)	K_2	R_2^2	D_2 (cm^2/s)
1	65	0.156	0.0236	0.9349	5.64E-02	0.0084	0.9953	7.15E-03
2	500	1.2	0.0161	0.9546	4.44E-04	0.0602	0.9979	6.20E-03
3	862	2.0688	0.3035	0.9224	5.30E-02	0.0712	0.9963	2.92E-03
4	1378	3.3072	1.0138	0.8548	2.32E-01	0.0503	0.8586	5.70E-04
5	3200	7.68	1.2369	0.9262	6.39E-02	0.0579	0.9622	1.40E-04

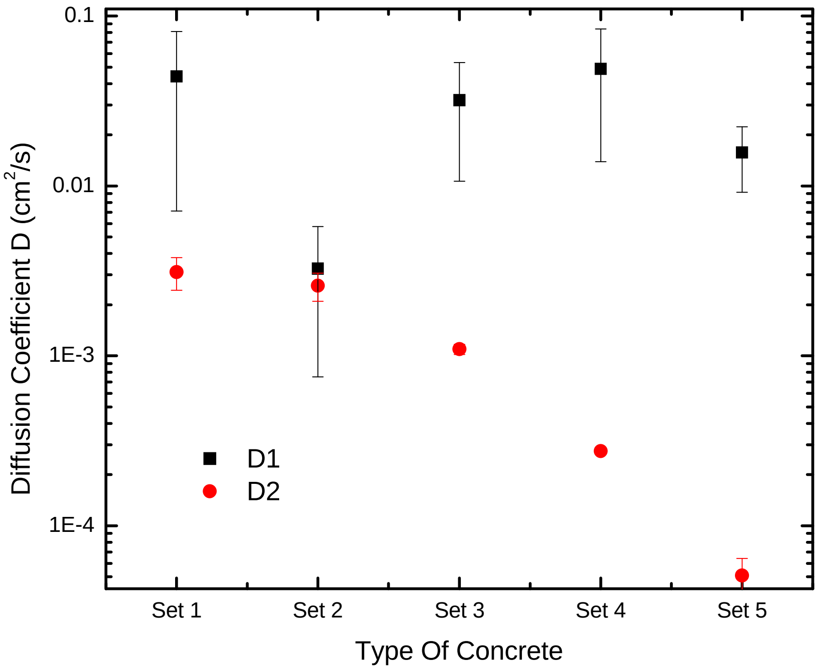

Figure 14: Diffusion Coefficients of the 5 Sets of Concrete in the First 8-hr Mixing and Curing Period

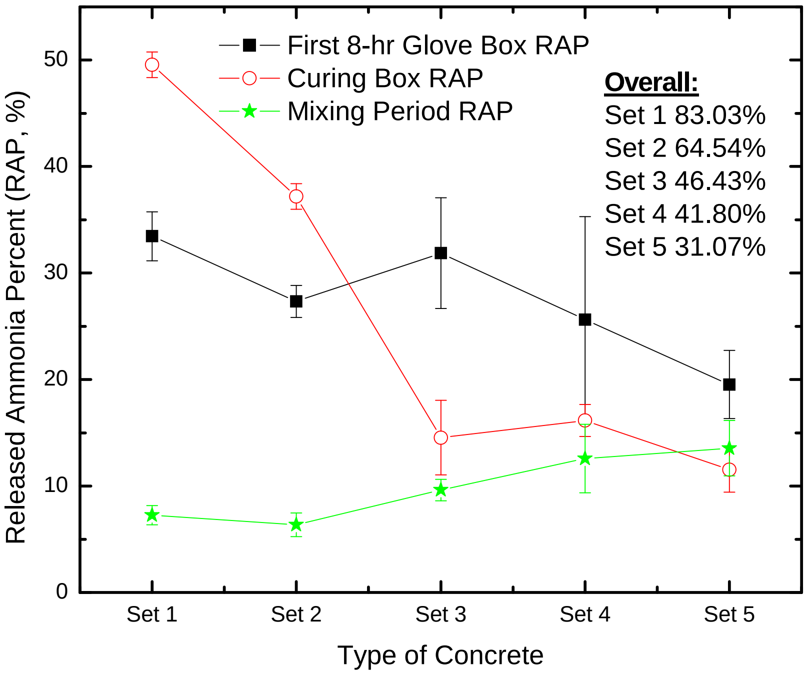

Figure 15: Released Ammonia Percentage (RAP) of the 5 Sets of Concrete in the First 8-hr Mixing and Curing Period

8.2.2. Curing Box Experiment

Ammonia release decreased consistently during daily monitoring. Results for curing box experiment are shown in Figure 16. For different concrete sets, it took different time for all ammonia to be released from the concrete. As shown, after 5 days, the daily release of ammonia from concrete set 1 (with AFA Type A) was out of the detection limit of the IC, which means diffused ammonia concentration from the surface of the concrete is lower than 500 ppb level. For the concrete set 5 (with AFA Type E), it took 18 days to be out of the detection limit of the IC. Most ammonia was released in the first 24 hours when moist content of the concrete slab is still high. RAP of the entire curing period was shown in Figure 15.

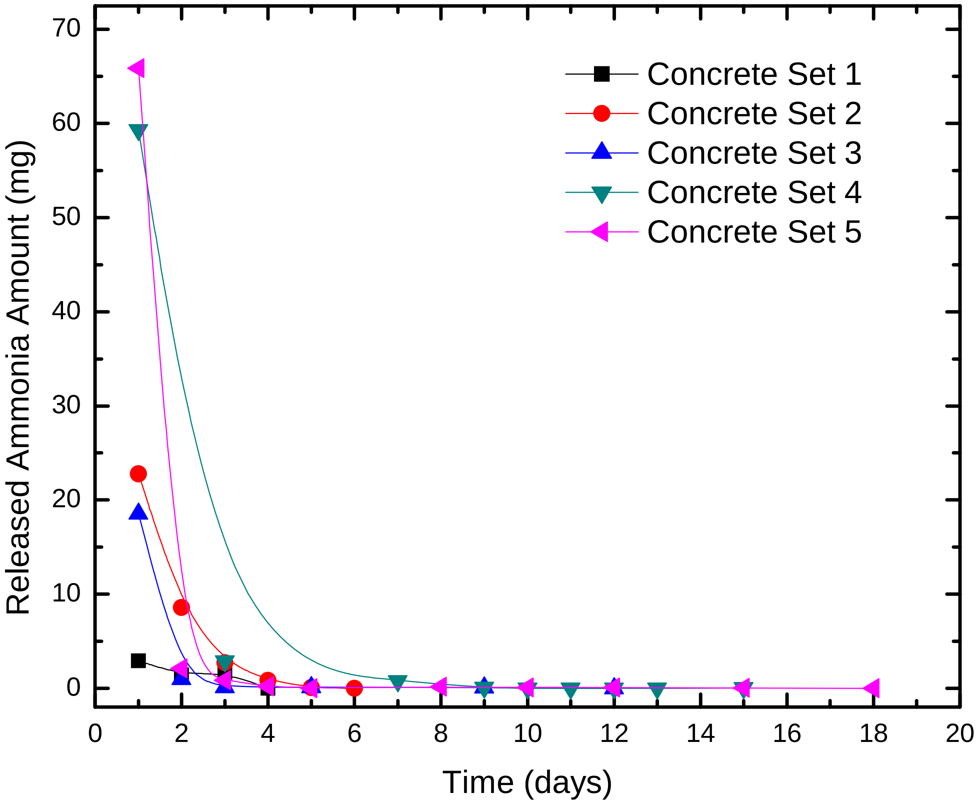

Figure 16: Released Ammonia Concentration within Curing Box

8.2.3. Discussion of Ammonia Volatilization

Concrete mixing and setting/curing period is a complex process which involves chemical reactions and physical structural changes to the concrete matrix. The major chemical reaction which causes the concrete to form its hardened state is called hydration, which occurs between the Portland cement and water.

Portland cement is a mixture of many compounds. Among these different compounds, tricalcium silicate and dicalcium silicate are the two most important compounds, which constitute about 75% of the weight of Portland cement and react with water to form calcium hydroxide and calcium silicate hydrate. The chemical reactions are shown below (Kosmatka et al., 2002):

$$\underset{\text{Tricalcium silicate}}{2(3CaO\cdot SiO_2)}+\underset{\text{water}}{11H_2O}\rightarrow\underset{\text{Calcium silicate hydrate}}{3CaO\cdot 2SiO_2\cdot 8H_2O}+\underset{\text{Calcium hydroxide}}{3Ca(OH)_2} \tag{35}$$

$$\underset{\text{Dicalcium silicate}}{2(2CaO\cdot SiO_2)}+\underset{\text{water}}{9H_2O}\rightarrow\underset{\text{Calcium silicate hydrate}}{3CaO\cdot 2SiO_2\cdot 8H_2O}+\underset{\text{Calcium hydroxide}}{Ca(OH)_2} \tag{36}$$

Secondarily reactions will occur between calcium hydroxide, pozzolanic material and water to form calcium silicate hydrates, which is shown in the following process:

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2}+Pozzolan+H_2O\rightarrow\underset{\text{Calcium silicate hydrate}}{3CaO\cdot 2SiO_2\cdot 8H_2O} \tag{37}$$

Calcium silicate hydrate, the newly formed compound in the chemical reactions, is the heart of the concrete. Various engineering properties of the concrete, such as hardening, strength and dimensional stability, depend mainly on this hydrate. The hydration process occurs both in mixing and curing periods of concrete. Pore spaces within the concrete mixture are filled by calcium-silicate hydrates as concrete cures and ages.

In the concrete mixing process, since water is combined with the cement, ammonium salts, such as ammonium sulfate and ammonium bisulfate which are adsorbed to the surface of the fly ash, are dissolved into the mixing water to create ammonium ions. At the same time, the hydration process between cement and water creates a high pH environment, which converts ammonium to ammonia that is subsequently released into the air. The reaction is based on the following equation:

$$NH_4^+ + OH^- \leftrightarrow NH_3\uparrow + H_2O \tag{38}$$

Note high pH shifts the equilibrium to the right.

This release process not only occurs on the bleed water surface of the concrete, but also proceeds in the porous structure of the concrete. However, as the pore spaces are filled during the concrete curing process and the concrete is dried, ammonia releasing rate will decrease and gradually approaches zero. The experimental data of this study verified this process. As shown in Figure 12, for all 5 sets of experiments (each set had a different ammonia concentration in fly ash and increased from 65 ppm in Set 1 to 3200 ppm in Set 5), cumulative mass release of ammonia per area tended toward equilibrium with time. It took up to 3 weeks for ammonia release to cease from the concrete slab. However, over 90% of ammonia which was released was released in the first day. Therefore, in considering workers' exposure to ammonia gas, modeling the ammonia release behavior during the first day should be the focus.

The dominant driving force for ammonia release is different for the concrete mixing and curing periods. In the mixing period, since a mixing truck or a person is continuously mixing the concrete, convection occurs between the water in the concrete and the atmosphere, which promotes ammonia release into the air. Diffusion has a driving force due to the concentration gradient of ammonia between the concrete mixing water and the air, which is another major mechanism that causes ammonia release. In this initial mixing process, the mass release rate should be greater than that caused by diffusion alone. It should be noted that the mixing rate will change the mass transfer rate in this initial mixing period.

After the mixing process, the concrete will be unloaded from the mixing truck/device to a place for setting and curing. In this process, no macroscopic motion is occurring. The driving force for ammonia release from concrete to the atmosphere is ammonia concentration gradient (pH of the concrete water will remain between 11 and 13 during this process). However, the concrete is drying, and pores are filled by hydrates and carbonate precipitates as concrete cures, which means the resistance for ammonia in the concrete water to be released into the air is increasing with time. According to Glicksman, 2000, the rate of transformation depends on the combination of the two kinetic factors: net driving force and process resistance. As concrete cures, the driving force (concentration gradient) is decreasing, and the process resistance is increasing with time. So, the overall mass release rate of ammonia is decreasing. Likewise, the diffusion coefficient D will decrease with time.

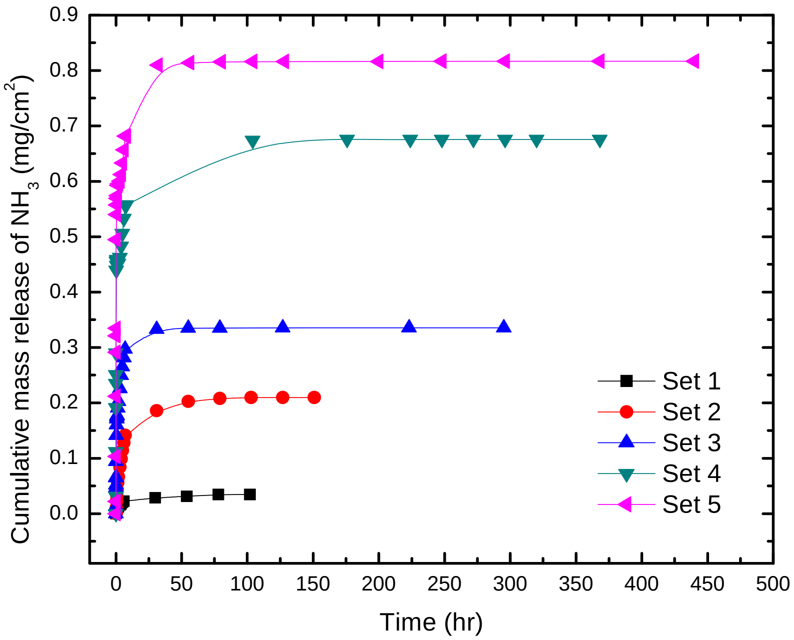

Figure 17: Cumulative Mass Release of Ammonia with Time

As shown in Figure 14, the overall diffusion coefficient of the first period (mixing period), D_1, is one to two orders of magnitude larger than that of the second period (curing period), D_2. At the beginning of the curing period, there is a formation of bleed water at the surface of the concrete. It is caused by sedimentation of solid particles (cement and aggregate) and the upward movement of water. As long as the concrete remains sufficiently moist, the diffusion coefficient can maintain relatively constant for a certain period. As shown in Figure 12, in the 10th min to 8-hour curing period, the cumulative mass release increases proportionally with square root of time. This shows that the diffusivity of this period is relatively constant.

In a later period, moist content of the concrete drops and the diffusion coefficient decreases over time. Drying rate of concrete depends on environmental conditions, concrete dimensions and concrete properties (Kosmatka et al., 2002). Usually the concrete closest to the surface dries quicker than the interior. When the moisture content in the concrete drops below 80%, the hydration process and strength gain of the concrete stops (Kosmatka et al., 2002). In addition, as moisture content decreases, more ammonium in the concrete will be stored as ammonium salts. The moisture content decreases from 100% to 80% typically in several weeks to 2 months (Kosmatka et al., 2002). The ammonia release rate results from the University of Kentucky and this study support such a phenomenon. That is, after a sufficient period, the ammonia release rate is so small that it is difficult to detect. In addition, in Figure 15, it is shown that the overall released mass fraction of ammonia in the entire mixing hardening process is smaller for a larger initial ammonium concentration in the concrete/fly ash, which can also be explained by the increasing ammonia release resistance of the concrete slab. In contrast, in the first 10-min mixing period, released mass fraction of ammonia is larger for a larger initial ammonium concentration in the concrete/fly ash, which proves that convection is a significant mechanism of the ammonia release rates in this period.

8.3. Ammonia Leaching

8.3.1. Synthetic Precipitation Leaching Procedure Results

The results from the SPLP test can be seen in Figure18 below. The results from the SPLP test can be graphed as a linear plot against total initial ammonium concentration in the concrete samples. When compared to GCTL for ammonia, a leachability threshold estimate can be determined for the material. This threshold is used as the site specific soil cleanup target level (SCTL) for the protection of groundwater (FDEP, 2009). This relationship indicates that the site specific SCTL is approximately 85 ppm of ammonium in concrete; which for this concrete mix design is equivalent to using a fly ash with an ammonia content of 850 ppm.

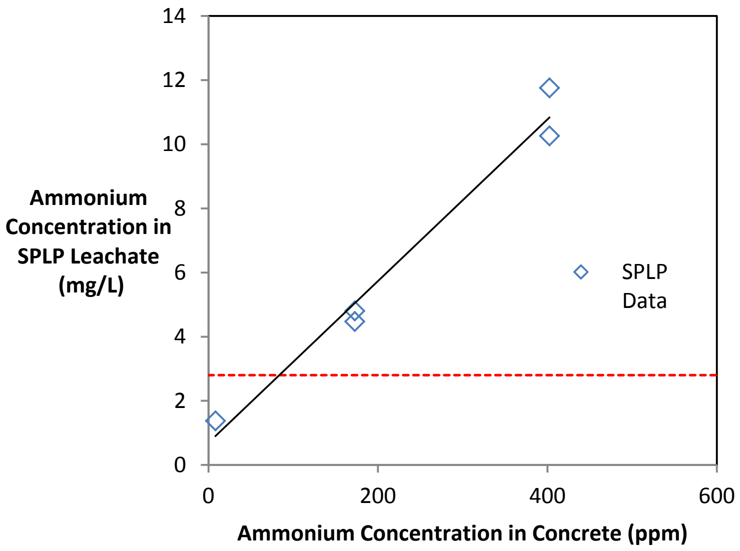

Figure 18: SPLP Results as Compared to Total Ammonium Concentration in Samples

8.3.2. Monolith Leaching Experimental Results

As expected, ammonium was released from all the monoliths during each leaching interval. This release is represented cumulatively in Figure 19. The total mass of ammonium leached was higher in samples with more ammonium initially present in the concrete matrix.

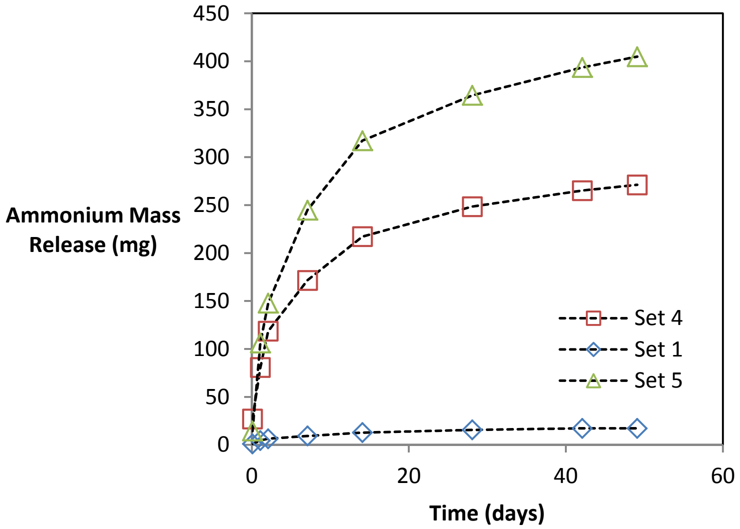

Figure 19: Cumulative Release of Ammonium from Concrete Monoliths

Additionally, larger ammonium mass flux rates were observed for samples with higher initial ammonium concentration. Evidence of this statement can be seen in Figure 24. However, as a total mass fraction of ammonium leached, the lower initial ammonium concentrations leached a higher fraction of total ammonium present initially. This is not surprising since less ammonium was initially available to leach but the ammonium leached at a similar rate in samples with low initial ammonium concentration as to the leaching rate in samples with higher initial ammonium concentration. This resulted in an accelerated depletion rate in samples with lower initial ammonium concentration, see Figure 20.

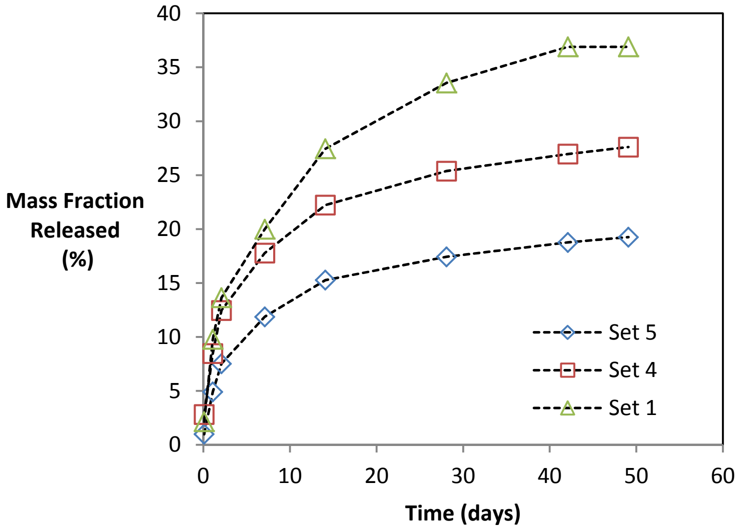

Figure 20: Mass Fraction of Ammonium Released from Concrete Monoliths

The observed diffusivity of ammonium for each set of samples can be seen in Figure 22. The diffusivity showed a clear trend of decreased diffusivity with increased initial ammonium concentration. It is important to note that the diffusion coefficients decreased with leaching time. This is due to two separate phenomena: source depletion and decreasing concrete permeability. The decrease in hydraulic permeability of concrete as a function of curing age is well documented (PCA, 2002).

The logarithmic representation of ammonium flux (Log [J_t]) and time (Log [t]) can be utilized to determine the dominant leaching mechanism during leaching intervals (Barna et al., 1997; Cheng and Bishop, 1990; Torras et al., 2010). If the data can be represented as a straight line with a slope > 0.65 the dominant leaching mechanism is surface dissolution; however, if the data have a straight line slope between 0.35 and 0.65, diffusion is the dominant mechanism. Depletion is indicated if the slope of the line is less than 0.35 in later leaching periods (Torras et al., 2010). As can be seen in Figure 21, the dominant leaching mechanism during the initial leaching intervals is diffusion. The initial data point was excluded since this was likely skewed due to initial surface wash-off of ammonium. During later periods, i.e. > two weeks, the leaching mechanism is due to a residual diffusional release since the source of ammonium has been effectively depleted (Garrabrants et al., 2010).

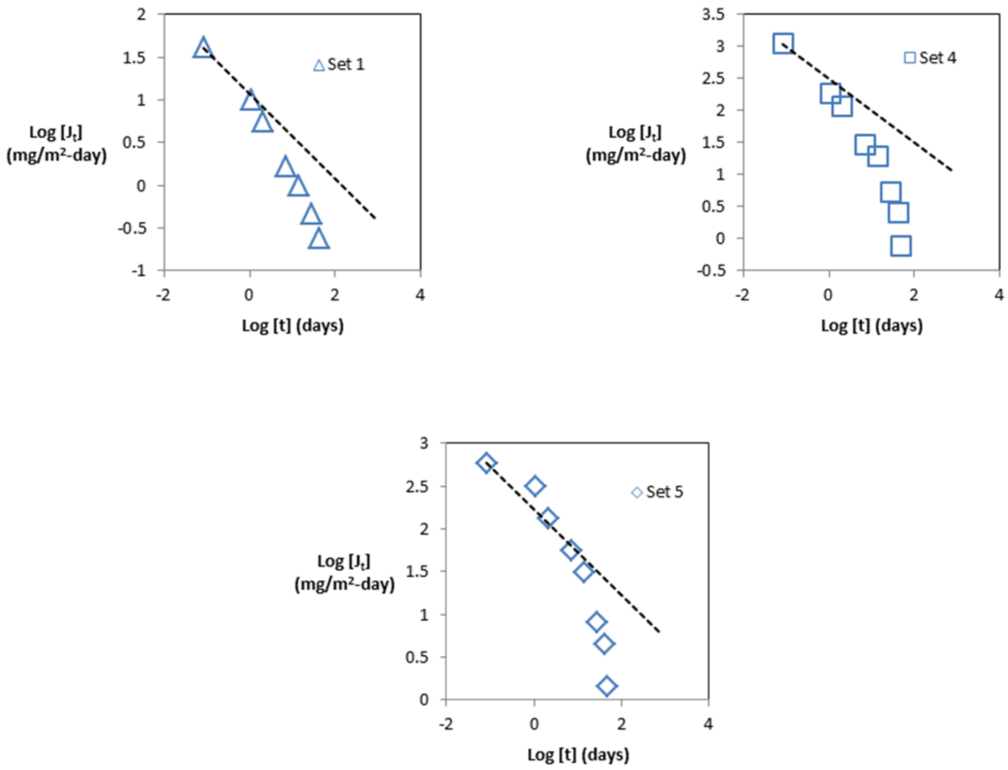

Figure 21: Log [J_t] vs. Log [t], Where the Straight Line is of Slope -0.5

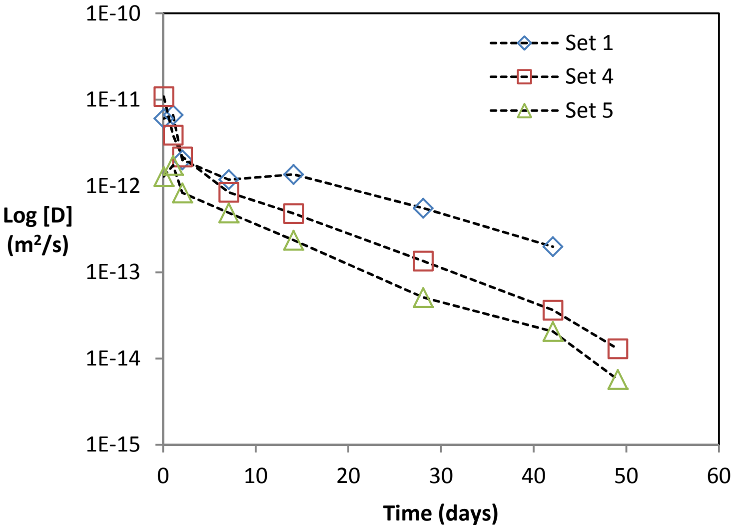

Figure 22: Observed Diffusivity of Ammonium in Concrete Monolith Specimens

The fact that the diffusion coefficient does change with time is an indication of the limitation of the semi-infinite diffusion model. However, as previously mentioned, the semi-infinite diffusion model is widely used and practical. Due to these observations, separate mean diffusion coefficients for the two leaching mechanisms, i.e. diffusion mechanism (D_1; < two weeks) and residual diffusional release (D_2; > two weeks), can be developed for each set of samples, as seen in Figure 23. These diffusion coefficients can then be used to model theoretical mass releases of samples identical to the samples used in the leaching procedure, i.e. proof of model efficacy, or samples with different dimensions and initial ammonium concentrations.

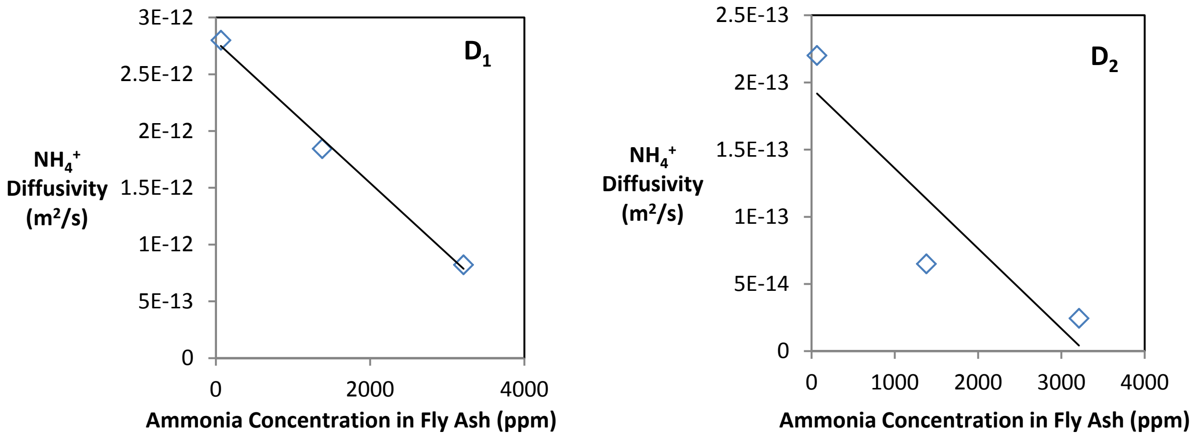

Figure 23: Mean Diffusivity for Initial Diffusion Rate and Residual Diffusion Rate

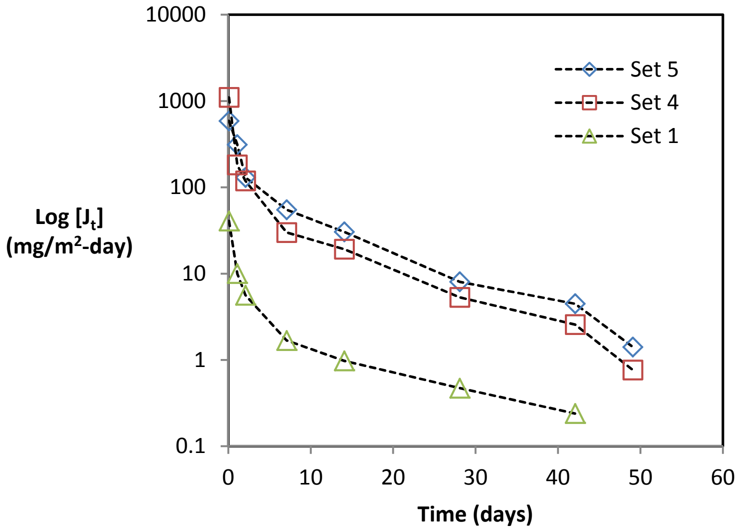

Figure 24: Measured Ammonium Flux during Interval Leaching of Concrete Monoliths

8.3.3. Discussion of Leaching

As an initial estimate of ammonium release risk to the environment, a mass balance assessment was completed, as can be seen in Section 6.3.1: Potential Ammonia Release to Soil and Water. As part of this preliminary assessment, it was shown that initial ammonia contained in concrete samples would never exceed SCTL (Soil Cleanup Target Level) for ammonia at any assumed soil pH values. Therefore, concrete amended with any ammoniated fly ash at ammonia concentrations determined during the literature or industrial review, i.e. 0 – 3200 ppm, would be of no concern to direct human exposure in residential or industrial settings.

However, to determine if the use or reuse of concrete amended with ammoniated fly ash would be a concern for the protection of groundwater, SPLP results were compared to initial ammonium content of concrete samples. Since the concrete mix design chosen for our samples was designed such that ammonia concentration in the concrete was maximized, these ammonia concentration values in concrete are directly comparable to ammonium concentration in fly ash. From the analysis of the SPLP results, it was determined that a leachability threshold of 850 ppm of ammonium in fly ash is proposed for the protection of groundwater.

From the experimental results of the monolith leaching test, it is clear that the average diffusivity for ammonium for the two leaching mechanisms can be used to predict ammonium release rates of other concrete monolith dimensions and initial ammonium concentrations. It is not unrealistic to use the semi-infinite model for this predictive purpose since the model is independent of monolith dimensions, as can be seen in Equation 19. As a proof of model efficacy, the initial ammonium concentration of the monolith samples used in the original leaching tests and mean diffusivity for both leaching regimes were used to predict cumulative mass release of ammonium. The initial ammonium concentration used can be seen in Table 21. Additionally, this was done for three different simulated initial concentrations of ammonium, see Table 23. The simulated release was compared to measured values, as can be seen in Figure 25. The results of the simulated samples, i.e. sets A – C, can be seen in Figure 26.

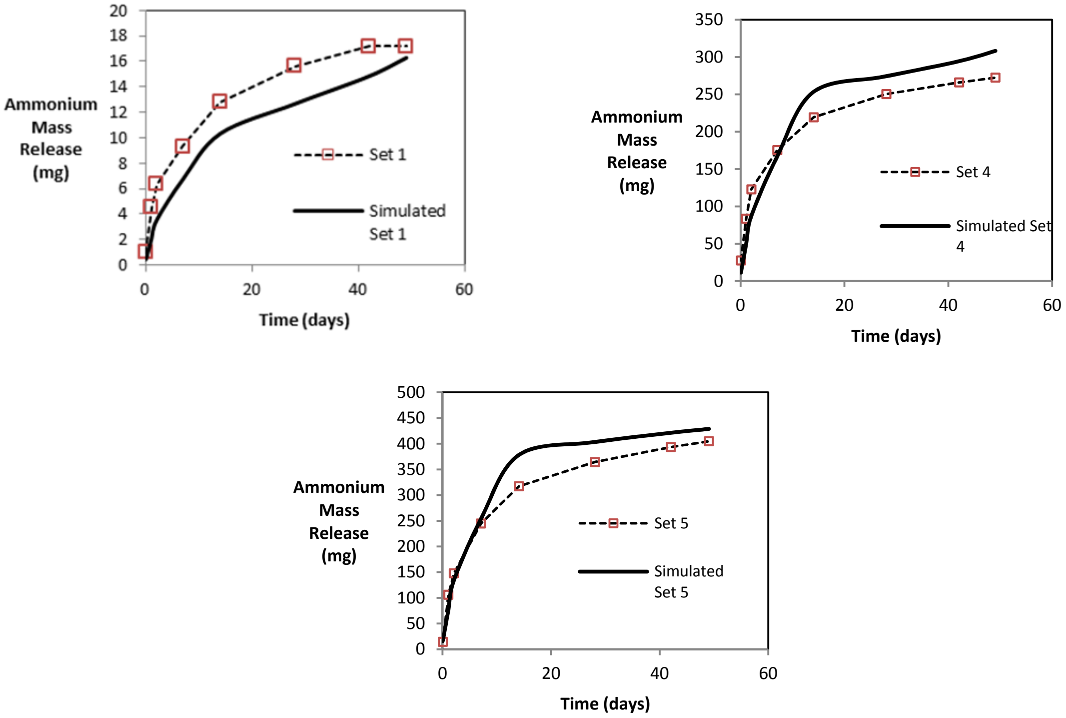

Figure 25: Measured Cumulative Ammonium Mass Release and Simulated Ammonium Mass Release

Table 23: Simulated Sample Sets

Sample Identification	Calculated Diffusivity (m^2/s)		Initial Ammonium Concentration in Fly Ash (ppm)
	D_1	D_2	
Set A	2.88×10^{-12}	1.88×10^{-13}	200
Set B	2.70×10^{-12}	1.70×10^{-13}	500
Set C	2.40×10^{-12}	1.40×10^{-13}	1000

Since the mass release (mg/m^2) can be calculated for any time during the leaching period, it is also possible to calculate the mass flux rate (mg/m^2-day) for any time period as well. It is critical to determine the maximum mass flux rate at any time period during leaching since this value will be compared to regulatory limits, e.g. SWCTL.

A worst-case scenario can be presented to calculate a conservative estimate of a leachability threshold concentration in fly ash for the protection of surface water from ammonium leaching from concrete amended with ammoniated fly ash. Imagine a stagnant water body, such that no convective movement of leached ammonium can occur, then the leached ammonium would diffuse out from the concrete interface a specified distance due to Brownian motion. This distance can be predicted by the following relationship:

$$x = 2\sqrt{D_{NH4}t} \tag{39}$$

Where x is the distance the ammonium would travel in time t and D_{NH4} is the diffusion coefficient of ammonium in water, i.e. 6.93 x 10^{-9} m^2/s. Therefore, the distance ammonium can diffuse out from a concrete surface with the previously mentioned assumptions is 0.05 m. The most typical geometric concrete form used by the FDOT is the cylindrical shape of bridge pilings. Assuming a cylindrical geometry, the volume of water that ammonium leached from the concrete can be calculated. Additionally, the cylindrical geometry surface area can be calculated and a liquid to surface area ratio (L/SA) can be determined. It should be noted that despite changes in the magnitude of dimensions of the cylindrical geometry the L/SA will remain constant at 50. Therefore, for all further calculations an L/SA ratio equal to 50 will be assumed.

As can be noted in Figure 24, the maximum interval flux occurred after the first 2 hours. It is noted that the initial flux rate was higher; however, it was not used since it is likely an artifact of the method of curing the concrete samples resulting from initial wash-off of surficial ammonium. The flux rate after 2 hours can be used to predict the instantaneous peak concentration in the scenario presented previously, i.e. diffusional release of ammonium from a concrete bridge piling by the following relationship:

$$C_{max} = \frac{J}{L/SA} \tag{40}$$

However, to directly compare these calculated values with the SWCTL (Surface Water Cleanup Target Level) for ammonia, the total unionized ammonia concentration must be determined from the calculated ammonium concentration. The Florida Department of Environmental Protection (FDEP) provides guidance to determine unionized ammonia as a fraction of total nitrogen ammonia, i.e. total unionized (NH_3) and ionized (NH_4^+) ammonia, using the following expression (FDEP, 2001):

$$f = \frac{1}{(10^{pKa-pH})} \tag{41}$$

Where pK_a is the acid dissociation constant for ammonium and f is the fraction of unionized ammonia. The simulated maximum instantaneous unionized ammonia concentration can be compared to initial ammonium concentration in fly ash used for each sample in Figure 26. As can be seen, there is a clear linear relationship between maximum instantaneous unionized ammonia concentration and initial ammonium concentration in fly ash. From this relationship a threshold leachability concentration can be determined for the protection of surface waters with respect to ammonia, see Figure 27. Based on this analysis, the leachability threshold concentration is 940 ppm of ammonium in fly ash.

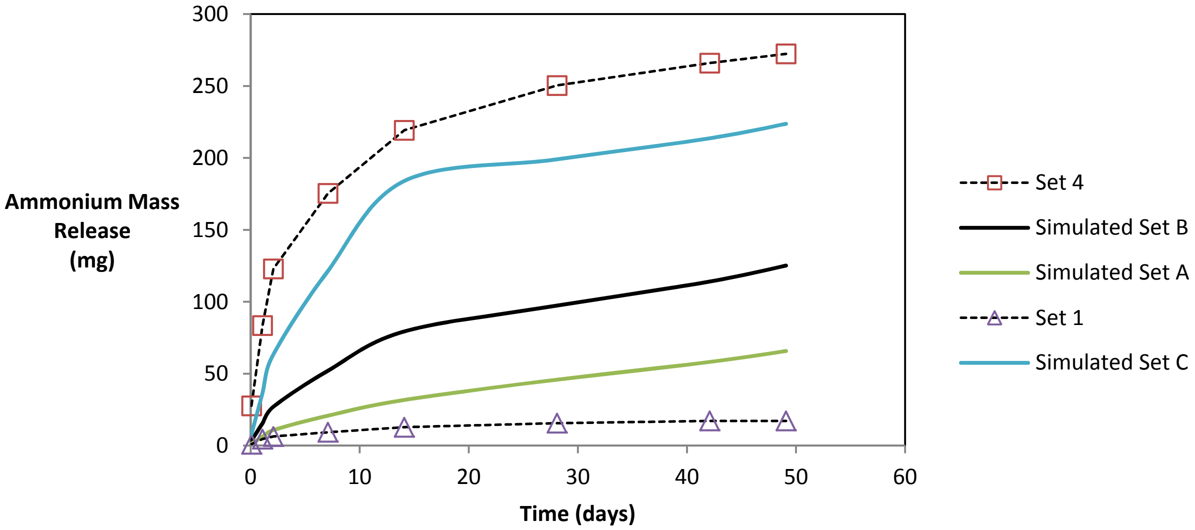

Figure 26: Measured and Simulated Mass Release of Various Initial Ammonium Concentrations

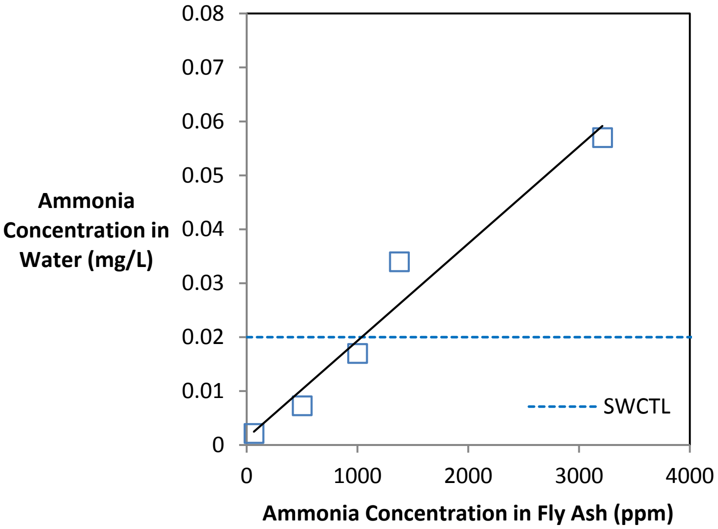

Figure 27: Comparison of Peak Un-Ionized Ammonia Concentration to Fly Ash Ammonium Concentrations

8.4. Summary of Results

Diffusion/mass release coefficients of ammonia in concrete are not constant values. They will decrease with time. The first reason is due to physical and chemical changes of the concrete. The hydration process is proceeding during the entire mixing and curing process. Calcium silicate hydrates formed during chemical reactions fill the pore space of the concrete which leaves fewer pathways for ammonium to diffuse out. In addition, the moisture content of the concrete will decrease as the concrete ages, which also prevents ammonium ions from diffusing into the ambient environment. During the mixing period, ammonia release is enhanced due to continuous mixing. The diffusion coefficient of this period is the highest. During the curing period, diffusivity is relatively constant for the first several hours, since the moisture content of the concrete remains high. However, when the moisture content decreases the diffusion coefficients start to decrease quickly.

According to the experimental results, over 90% of ammonia release occurs in the first day; later periods show significantly decreased ammonia release rates. Since the focus of the study is workers' ammonia exposure level, the first 8-hr ammonia release behavior should be modeled and time-weighted average (TWA) exposure value will be calculated in the following sections to compare with OSHA and NIOSH standards.

The leaching experimental results suggest that release of ammonium from hardened concrete samples is primarily a concern during the first two weeks of placement. After this initial diffusional release, the release rates for ammonium decrease significantly and will not be a concern to the environment. Based on the peak release rates, i.e. occurring within the first 2 hours, a leachability threshold value for ammonia content in fly ash has been proposed for the protection of surface water. This estimate is based on the assumption that concrete structures amended with ammoniated fly ash will be placed directly into a static surface water body. Based on the diffusional release of ammonium from concrete, the maximum concentration level of ammonia in fly ash is set at 940 ppm. However, for the protection of ground water the maximum advisable level of ammonia in fly ash to be used in FDOT concrete mixes is 850 ppm.

9. Exposure Assessment and Recommendations

9.1. Assessment Objective

A semi-infinite diffusion model was developed to interpret experimental data, and diffusion coefficients of different concrete mixing/curing periods were obtained. In practice, working conditions vary during concrete handling, mixing and finishing at job sites. To estimate workers' ammonia exposure in practice, typical cases in which worker exposure can be potentially high are described, including outdoor concrete construction, placing concrete into a form with high walls, concrete ready-mix truck and in a room with or without ventilation. In each scenario, working conditions such as the amount of concrete used, mixing time and wind velocity greatly affect workers' ammonia exposure level. Therefore, to effectively use analytical models to evaluate the exposure, reasonable working conditions need to be assumed for each scenario.

In the following sections, four scenarios are described and assumptions of working conditions are listed in corresponding tables. For each scenario, in order to facilitate calculation, values were assumed for general parameters such as concrete density and mass of concrete to be used. Key environmental and operating parameters that can affect the exposure levels, such as wind speed and concrete mixing time, were then varied to obtain the relationship between ammonia concentration in air (8-hr Time Weighted Average value) and ammonium concentration in concrete/fly ash. Time Weighted Average (TWA) ammonia concentrations in the air were compared with OSHA PEL and NIOSH REL standards. Finally, a worker safety threshold for ammonia concentration in fly ash/concrete was recommended.

9.2. Exposure Models

9.2.1. Scenario 1: Constructing an Outdoor Concrete Slab, Roadway or Bridge Deck

In this scenario, workers place concrete into a slab form and finish the concrete slab in an open environment, as shown in Figures 28 and 29. Data from the lab experiments indicate that the rate at which ammonia is released during the process of mixing, placing and consolidating is higher than the rate at which ammonia is released during the concrete finishing period. Therefore, two emission rates were used in the model. Assumptions used in the model are listed in Table 24.

Ammonia will quickly disperse into the atmosphere during the construction of an outdoor slab, roadway or bridge deck. Even wind of a low velocity will enhance dispersion. Examples of this scenario are construction of a concrete slab, a roadway section and a bridge deck. Photos of these working conditions are shown in Figures 29 a) and b), respectively. Zero wind speed is the worst-case scenario for exposure of the workers to ammonia. The diffusion mechanics in the bridge deck placement were the same as that in the roadway pavement case, except that wind velocity is usually higher on a bridge and more air tends to move around the workers so that the ammonia exposure level should be relatively lower.

Concrete is usually delivered in a ready-mix truck that is driven on the road for up to an hour. During this period, workers are not exposed to the ammonia that is released from the truck. In the model, this period was assumed to be a "transportation/mixing period". Ammonia released from the truck during this period was not included when calculating a worker's 8-hr Time Weighted Average (TWA) exposure value. The transportation/mixing time was varied to evaluate workers' exposure level to ammonia after various amounts of ammonia had been lost in transit, as shown in Table 24.

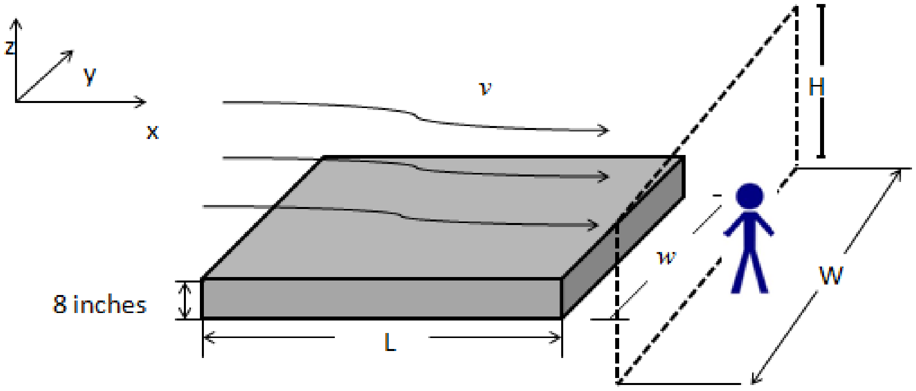

Figure 28: Workers Around a Freshly Placed Concrete Slab in an Open Environment

a) Roadway Placement (Roadway Access Ramps, 2012)

b) Bridge Deck Placement (Memorial Bridge)

Figure 29: Examples of Scenario 1

Table 24: Assumed Parameters in Scenario 1

Scenario Parameters	**Assumed Values**
Concrete density	2400 kg/m^3
Volume of Concrete	6.88 m^3 (9 cubic yards)
Concrete thickness	20.32 cm (8 inches)
Dimensions of the concrete slab[1]	6.72 m (L) ×5 m (W)
Mass fraction of cement in concrete	20%
Mass fraction of fly ash in cement	50%
Placement time	30 min
Ammonia concentration in fly ash	0 – 200 ppm
Transportation/mixing time	0 – 1 hr (0 min, 30 min and 1 hr will be used for calculations)
Wind velocity[2]	1 – 6 m/s (1 m/s, 3m/s and 6 m/s will be used for the calculations)

[1] Dimensions of the concrete slab is decided according to the volume of the concrete and its thickness.

[2] Wind velocities of 1-6 m/s were selected from the Pasquill Stability Class of Weather Tables.

In this scenario, a Gaussian dispersion model can be applied to estimate ammonia concentration downwind of the concrete slab (Turner, 1994):

$$C = \frac{Q}{4\pi x D_{NH_3\_in\_air}} \exp\left[-\left(\frac{y^2}{D_{NH_3\_in\_air}} + \frac{z^2}{D_{NH_3\_in\_air}} \right) \frac{u}{4x} \right] \quad (42)$$

A Gaussian dispersion model was used to describe diffusion at any point downwind of the emission, as shown in Figure 30. Assumptions of this model are as follows: 1) Mass transfer due to bulk motion in the x-direction far out-shadows the contribution due to diffusion; 2)

Continuous emissions; 3) Steady state conditions; 4) Constant wind velocity; and 5) Conservation of mass.

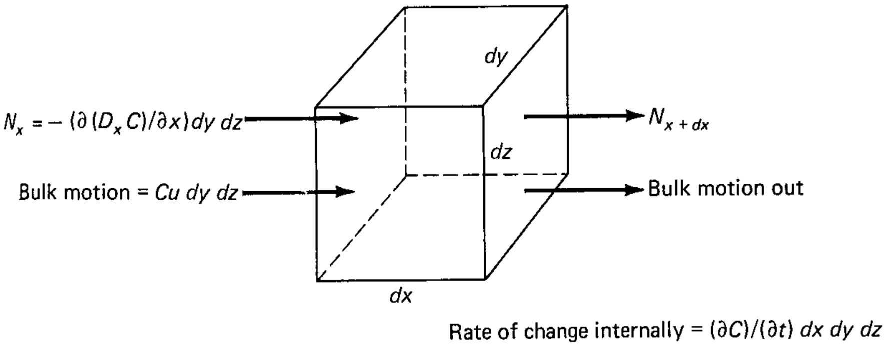

Figure 30: Dispersion Model in Scenario 1 with Wind

According to the Gaussian dispersion model, ammonia concentration right above the concrete slab (at the origin when x=0) approaches infinity, which is unrealistic. To estimate ammonia concentration above the concrete slab, mass balance in a control volume (V) can be written as:

$$\frac{\partial C}{\partial t} = \frac{m_{in} - m_{out}}{V} \tag{43}$$

Where m_{in} is the amount of ammonia generated by the concrete slab, m_{out} is the amount of the ammonia that goes out of the control volume. Since mass transfer due to bulk motion in the x-direction far out-shadows the contribution due to diffusion, the amount of ammonia diffused out of the control volume can be neglected. Assuming the control volume V = L (length) × W (width) × H (height), Eqn. (43) can be written as:

$$\frac{\partial C}{\partial t} = \frac{J \cdot L \cdot W - C \cdot u \cdot H \cdot W}{L \cdot H \cdot W} \tag{44}$$

or with further simplification as:

$$\frac{\partial C}{\partial t}=\frac{J}{H}-\frac{u}{L}C \tag{45}$$

Since *J* (flux of ammonia) is changing over time (as shown in Eqn. (17) in Section 7.3), Eqn. (45) should be solved numerically in the following steps:

$$\frac{C_2-C_1}{\Delta t}=\frac{J}{H}-\frac{u}{L}\left(\frac{C_1+C_2}{2}\right) \tag{46}$$

$$C_2-C_1=\frac{J\Delta t}{H}-\frac{u\Delta t}{2L}\left(C_1+C_2\right) \tag{47}$$

$$C_2=\frac{\frac{J\Delta t}{H}+(1-\frac{u\Delta t}{2L})C_1}{1+\frac{u\Delta t}{2L}} \tag{48}$$

Initial ammonia concentration in the control volume $C_{t=0} = 0$.

In order to compare modeling results with related regulations such as NIOSH PEL and OSHA which are 8-hr TWA values, the time weighted average concentration C_{TWA} in the control volume can also be calculated using the following equation:

$$C_{TWA}=\frac{\int_0^t C_t dt}{t} \tag{49}$$

The typical concrete slab thickness is 6 – 8 inches. Therefore, the total volume and surface area of the concrete slab can be calculated. Based on this information and an assumed wind velocity, the mathematical relationship in Equation 42 and 48 can predict the individual worker exposure.

9.2.2. Scenario 2: Placement of Concrete in a Form with High Walls

In this scenario, concrete is continuously pumped into a form with high walls as shown in Figure 31. Final placement of concrete in a footer is shown in Figure 32. Concrete consolidators working in a form with high walls often work right at the surface of the concrete as it is being placed in the form. Their job is to direct the placement of the concrete and vibrate the concrete to help the concrete flow around the rebar and get large air bubbles to be released from the concrete. If there is little or no wind blowing across the top of the form, ammonia can only exit from the top of the form to the ambient environment by diffusion. In this case, it is possible that relatively high concentrations of ammonia can develop inside the formed area.

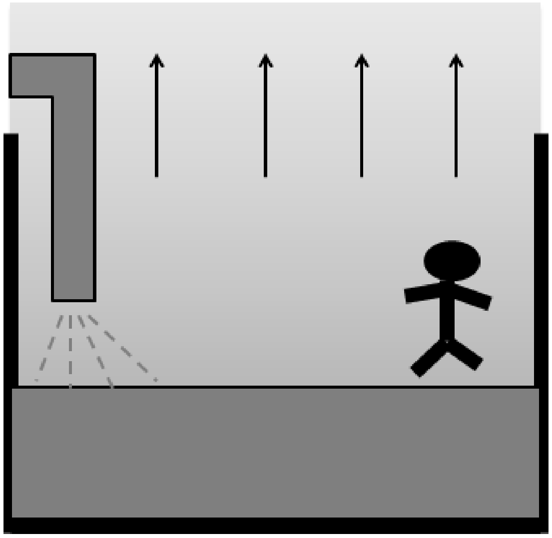

Figure 31: Placement of Concrete in a Form with High Walls

Figure 32: Example of Scenario 2 (City of Caribou, 2012)

Workers may be exposed to relatively high ammonia concentrations during this period. In our model, this placement/consolidating period is assumed to be 1 hour. The concrete pumping rate and the open area at the top of the form will affect the ammonia concentration in the air inside the form to a large extent. Typical pumping rates of 20 to 75 cubic yards per hour were considered. Wind velocity was assumed to be zero in this case. After all of the concrete is placed in the footer, the ammonia release rate decreases. The concrete finishers typically don't begin work until 30 to 45 minutes after the concrete is placed. During the finishing period, it was assumed in the model that workers would be exposed to a lower ammonia release rate. Assumptions used in the model calculation are listed in Table 25. The depth of a typical footer is usually 5 to 7 feet. Workers stand on the top mat of the reinforcing bar or on a construction bridge to finish most of the work. This case is much better than working at the bottom of the footer and is closer to the situation in Scenario 1.

Table 25: Assumed Parameters in Scenario 2

Scenario Parameters	**Assumed Values**
Concrete density	2400 kg/m^3
Mass fraction of cement in concrete	20%
Mass fraction of fly ash in cement	50%
Transportation/mixing period	0 – 1 hr
Placing/consolidating period	1 hr
Ammonia concentration in fly ash	0 – 200 ppm
Pump rate	20- 75 cubic yards/hr

In this scenario, since the concrete is pumped into a form with high walls, it can be simplified as a line source at the bottom of the form that continuously releases ammonia in the upward direction (y), as shown in Figure 33.

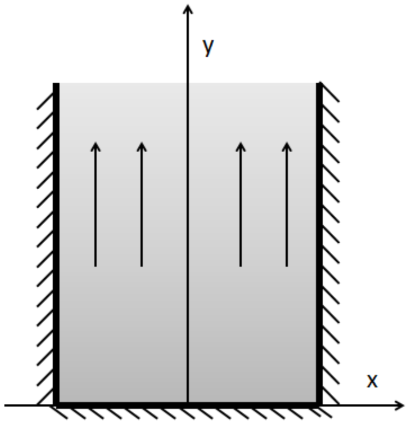

Figure 33: Diffusion Model for Scenario 2

Time and Distance Dependent Ammonia Concentration Can be Obtained with the Following Equation (Glicksman, 2000):

$$C(y,t) = 2\dot{m}\sqrt{\frac{t}{D_{NH_3\_in\_air}}}\left[\frac{e^{-y^2/4D_{NH_3\_in\_air}t}}{\sqrt{\pi}} - \frac{y}{2\sqrt{D_{NH_3\_in\_air}t}}\,erfc\left(\frac{y}{2\sqrt{D_{NH_3\_in\_air}t}}\right)\right] \tag{50}$$

where $\dot{m}$ is mass release rate; y is the vertical distance from the emission source.

9.2.3. Scenario 3: Ready-Mix Concrete Truck

As shown in Figures 34 and 35, for Scenario 3, workers unload a ready-mix concrete truck via the chute attached to the truck. In a worst case scenario, the ready-mix truck doesn’t allow the ammonia to off-gas. After the truck arrives at the site, the driver or other workers around the truck could be exposed to a high concentration of ammonia if he/she begins to unload the drum. In other cases when concrete is delivered using a dump truck the ammonia concentration in the concrete is lower than when it is delivered using a ready-mix truck.

In the model, a worst case situation was considered, i.e. there was no loss of ammonia from the truck. Ammonia diffused from the concrete was trapped in the headspace of the drum and the concentration in the headspace was calculated. The ratio of the total concrete volume to the volume of the drum is typically 1/2, which means that a typical ready-mix truck with a total volume of approximately 20 yd^3 is only filled to a maximum of 10 yd^3 of concrete in normal service. In practice, most ready-mix trucks in Florida only deliver 9 yd^3 of concrete as the total weight of the vehicle and concrete would be close to the maximum allowed weight (80,000 lbs) regulated by FDOT. The total mixing time for the concrete in the truck should be no longer than 90 minutes. Assumptions used in the model calculation are listed in Table 26. Ammonia concentration in the headspace of the concrete drum can be calculated as:

$$C_t = \frac{M_t \cdot A_{interface}}{V_{headspace}} \tag{51}$$

Where M_t is the cumulative release of ammonia mass; $A_{interface}$ is the surface area of the interface between concrete and air in the drum; and $V_{headspace}$ is the volume of the headspace of the drum.

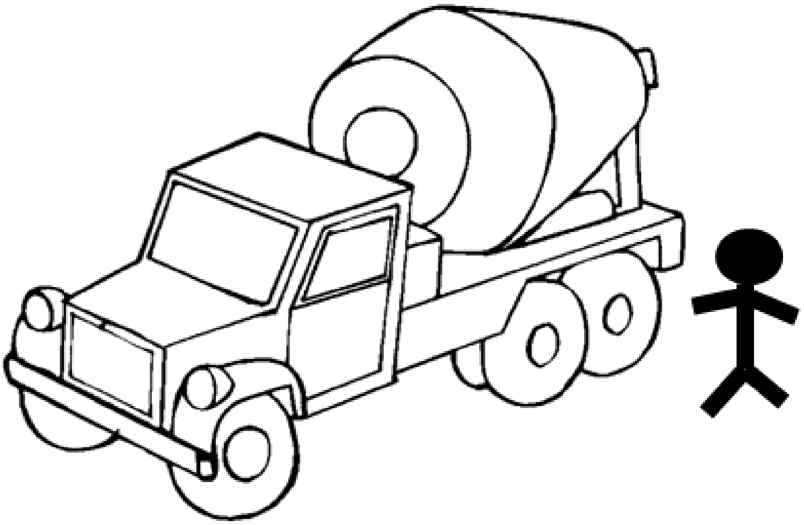

Figure 34: A Worker Near the Drum of the Concrete Mixing Truck

Figure 35: Example of Scenario 3 (Arizona Metro Mix, 2012)

Table 26: Assumed Parameters in Scenario 3

Scenario Parameters	**Assumed Values**
Concrete density	2400 kg/m^3
Concrete mixed	6.88 m^3 (9 cubic yards)
Concrete/Ready-Mix concrete truck volume ratio	0.5 (Truck Volume: 20 cubic yards; 3.7 m in length and 2 m in diameter)
Mass fraction of cement in concrete	20%
Mass fraction of fly ash in cement	50%
Ammonia concentration in fly ash	0 – 200 ppm
Concrete mixing time of the truck	0 – 1 hr

9.2.4. Scenario 4: Placement of Concrete inside a Building

This scenario considers an enclosed building where workers would pump concrete into the building with little or no ventilation occurring, as shown in Figures 36 and 37. Workers stay in the room for the placement and finishing of the concrete floor. In practice, concrete is mixed in a ready-mix truck outside the room on the way from the ready-mix plant to the site. Workers are not exposed to ammonia in this period and it was excluded in calculating workers' TWA ammonia exposure. After the concrete truck arrives at the site, the concrete is pumped into the room. A typical pumping period of 30 minutes for 9 cubic yards of concrete was assumed. After the pumping period and until the end of the 8th hour, workers would be exposed to ammonia at the lower emission rate. A constant fresh air flow rate, F, was assumed in this case. Constant and varied working conditions of Scenario 4 are listed in Table 27.

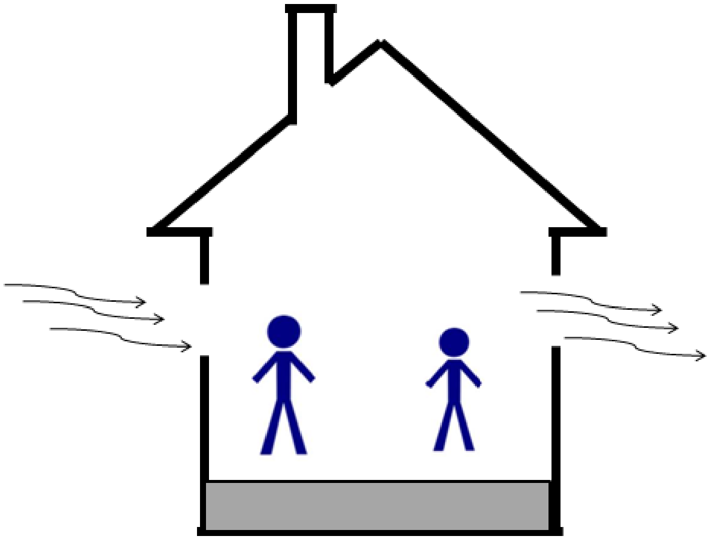

Figure 36: Workers Work in a Room with an Air Flow Rate F

Figure 37: Example of Scenario 4 (Smart Schools Clearinghouse, 2012)

Table 27: Assumed Working Conditions in Scenario 4

Scenario Parameters	Assumed Values
Concrete density	2400 kg/m^3
Concrete mixed	6.88 m^3 (9 cubic yards)
Concrete thickness	20.32 cm (8 inches)
Size of the room[2]	6.72 m (L) ×5 m (W) × 3 m (H)
Mass fraction of cement in concrete	20%
Mass fraction of fly ash in cement	50%
Workers involved	6 people
Minimum ventilation rate[1]	7.5 L/s per person
Placing time	30 min
Ammonia concentration in fly ash	0 – 200 ppm
Transportation/mixing period	0 – 1 hr
Ventilation rate	0 – 200 L/s per person

[1] Ventilation rate of 7.5 L/s per person is selected according to the minimum house ventilation rate specified in ASHRAE 62.

[2] Height (H) of the room is selected according to the typical ceiling height in practice; length (L) and width (W) of the room are decided according to the overall volume of concrete and concrete thickness.

Ammonia concentration at time t in the room can be calculated with the following mass balance equation:

$$\frac{\partial C_t}{\partial t} = \frac{M_t A + M_{in} - M_{out}}{V_R} \tag{52}$$

where $M_t A$ is the mass of ammonia released from the concrete inside the room, M_{in} is the mass of ammonia entering the room from non-concrete sources, which is assumed to be zero unless there is a specified source; M_{out} is the mass of ammonia leaving the room; and V_R is volume of the room. Assuming ammonia is instantaneously distributed throughout the room, the ammonia concentration of the air leaving the room is equivalent to that of air inside the room. Then M_{out} in a short time period Δt can be estimated by the following relationship:

$$M_{out} = M_t A\left(\frac{F\Delta t}{V_R + F\Delta t}\right) \tag{53}$$

where F is wind flowrate through the room, L/min. Substituting Equation 53 into Equation 52, the ammonia concentration in the room at time t can be estimated by the following model which can be solved numerically:

$$\frac{\partial C_t}{\partial t} = \frac{M_t \cdot A}{V_R + F\Delta t} \tag{54}$$

9.3. Exposure Assessment Result

9.3.1. Assessment Results of Scenario 1

In an open environment, even under stable weather, generally there is still wind going through the surface. Mass transfer due to wind in the downwind direction usually far out-shadows the contribution by diffusion. The mean gas displacement along any axis at time t by Brownian motion is (Hinds, 1999):

$$x = \sqrt{2D_{NH_3\_in\_air}t} \tag{55}$$

As shown in the equation, diffusing velocity caused by concentration gradient decreases with time. In the first second, the mean displacement of ammonia caused by diffusion is 0.675 cm. According to the record from National Oceanic and Atmospheric Administration (NOAA), monthly wind speed in Florida usually varies from 6 mph (2.68 m/s) to 14 mph (6.25m/s). Therefore, in an open field, gas displacement caused by the concentration gradient can be considered to be negligible in comparison with wind speed. Most ammonia released from the concrete slab will be diluted by wind immediately and will not be accumulated above the concrete slab. To estimate ammonia concentration just above the concrete slab, ammonia was assumed to be evenly distributed in a control volume of air just above the concrete slab. Depending on the assumed control volume, airborne ammonia concentration would be different. As discussed above, even when the wind velocity is as low as 1 m/s, diffusion speed is still much smaller compared with wind speed. Unless there is turbulent flow in the y and z directions, which is too complicated to be included in the simulation, it is unlikely that ammonia will diffuse a large distance from the surface of the concrete slab in these directions. Therefore, the control volume in this model was assumed to be the same length and width as the concrete slab (6.72 m ×5 m) and a variable effective height of 0.1, 0.3, and 0.5 m was used to estimate ammonia concentration above the concrete slab. The relationship between the initial ammonia concentration in fly ash, and ammonia concentration at the surface of the concrete slab is as shown in Figure 38. As shown in Figure 38 a (concrete mixed on site), since most ammonia is released during concrete mixing period, a threshold of ammonium in fly ash between 50 ppm and 80 ppm is recommended to meet NIOSH REL standard if concrete is mixed on site and workers are around the concrete. However, in practice, concrete is usually mixed in a ready-mix truck running on the road, and workers are not exposed to ammonia release. In these cases, modeling result in Figure 38 b and c should be closer to the actual situations. Ammonium concentration in fly ash lower than 100 ppm should be adequate for meeting OSHA/ACGIH/NIOSH TWA standards.

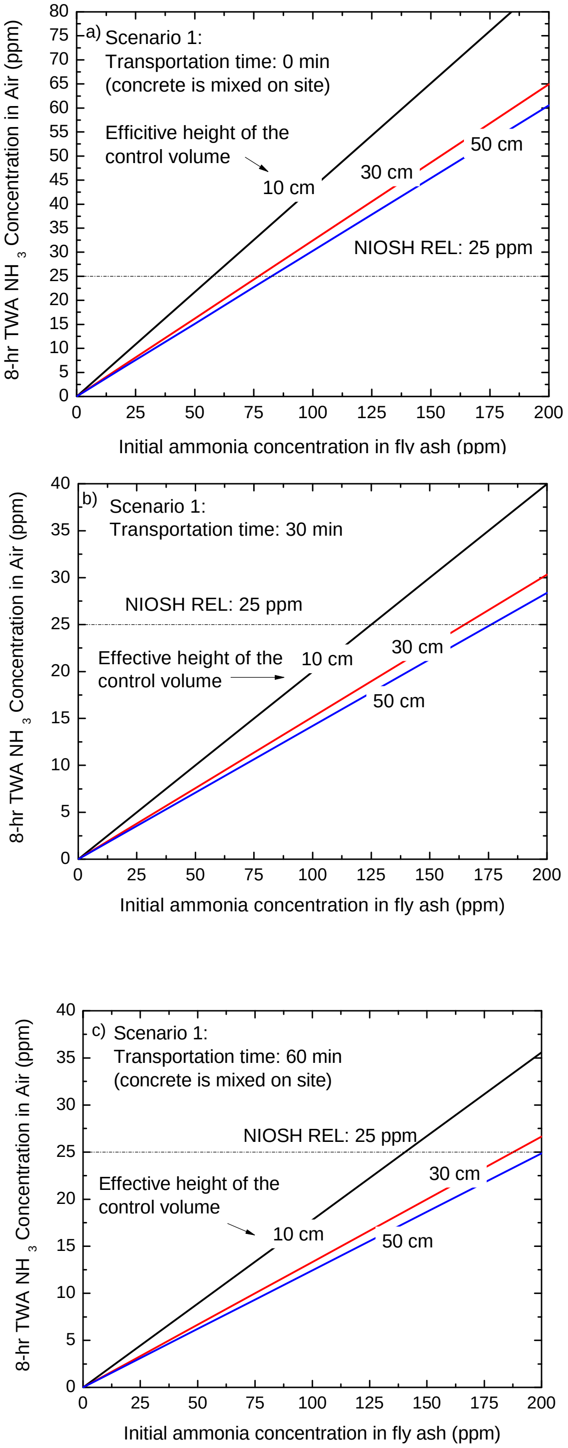

Figure 38: Initial Ammonia Concentration in Fly Ash vs. Ammonia Concentration in Air (Scenario 1 with Wind Velocity of 1 m/s)

The estimated results of downwind ammonia concentration are shown in Figure 39. As shown, the higher above the concrete surface, the lower ammonia concentration was. In both y direction and z direction, the tendency was the same. The highest ground level concentration always occurred along the centerline of the concrete slab. Even with a wind speed of 1 m/s, ammonia was quickly diluted by wind (even at the surface of the concrete slab). Ammonia concentration was lower than 1 ppm if the location was 200 m away from the emission source.

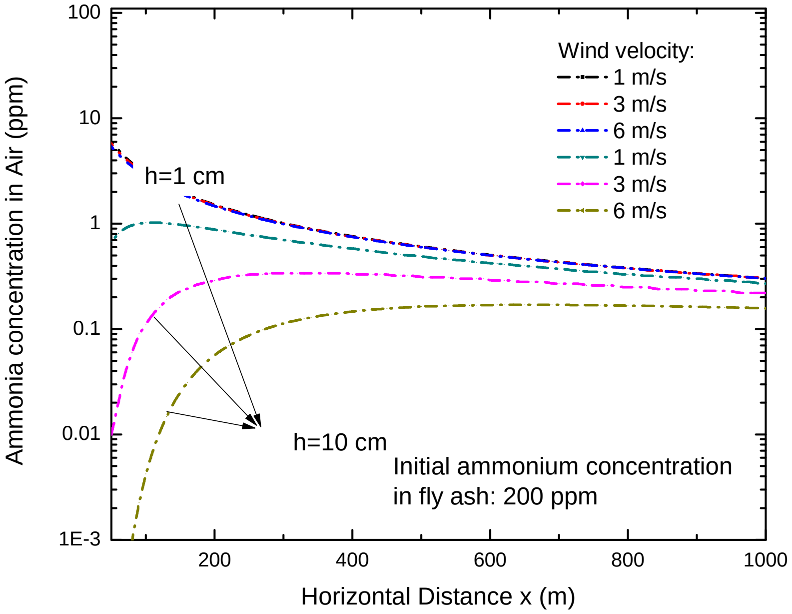

Figure 39: Ammonia Concentration Downwind the Concrete Slab at Various Wind Speeds

9.3.2. Assessment Results of Scenario 2

The modeling results are shown Figure 40. In this scenario, the assumption is ammonia can only diffuse in one direction and there is no wind in the form. Ammonia released from the concrete would be accumulated at the surface of the concrete slab and the concentration at the bottom of the form would be higher and higher as time goes on. Therefore, if no dilution air is provided from the bottom of the form, concrete consolidators can be exposed to a considerably high ammonia concentration if they need to stay at the bottom of the form. In practice, usually there are pieces of equipment such as fans to create wind to dilute the air in the form, in which, if the created wind speed is high enough, the situation would be similar to Scenario 1 with wind. In addition, the depth of a typical footer is only 5 to 7 feet (1.524 m to 2.13 m), ammonia can be quickly diluted by wind at ground level instead of accumulating in the form, which will make ammonia concentration closer to simulation results of scenario 1. For this complicated scenario, some field measurement is highly suggested.

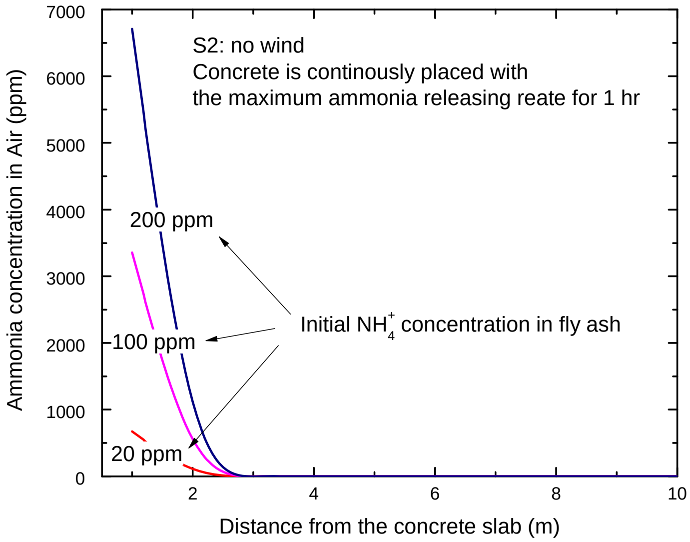

Figure 40: Ammonia Concentration in the Diffusion Field at the End of 1-hr Continuous Placement with the Maximum Ammonia Releasing Rate

9.3.3. Assessment Results of Scenario 3

In Scenario 3, the results of the worst case that all ammonia is trapped in the headspace of the ready-mix truck are shown in Figure 41. Since concrete was constantly mixed in the truck, if the lid of the truck was closed, ammonia continuously diffused to the headspace of the truck would be trapped and the concentration would be increasing with time. In general, concrete is mixed in a truck for 30 min to 1 hour. In addition, workers or drivers usually do not stay around the truck for a very long time. Hence, instant ammonia concentration instead of 8-hr TWA value was used to compare with NIOSH’s Immediately Dangerous to Life or Health concentration

(IDLH). As shown, if the initial ammonium concentration in fly ash was higher than 50 ppm, instant high ammonia concentration in the headspace of the truck could cause a danger to human health. In practice, as long as the lid is left open and ammonia can diffuse to the ambient air or be quickly diluted by wind through the opening, ammonia concentrations can be much lower than the simulated results.

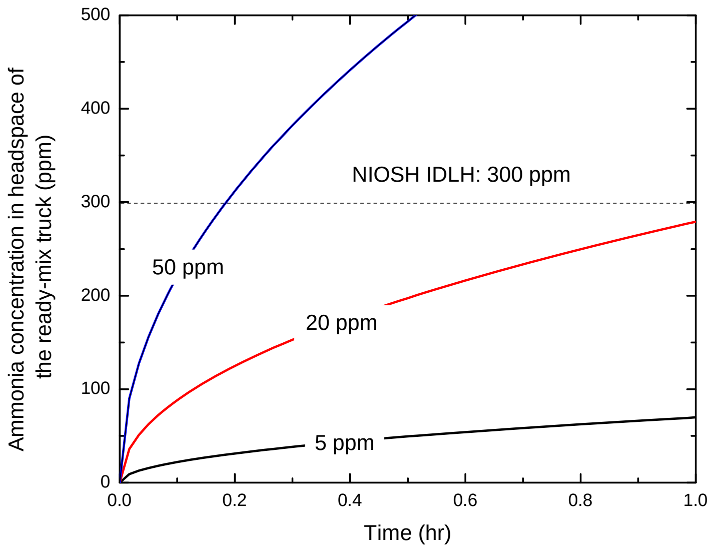

Figure 41: Ammonia Concentration as a Function of Time in the Headspace of the Ready-mix Truck (Initial Ammonium Concentration in Fly Ash Varies from 5 ppm to 50 ppm)

9.3.4. Assessment Results of Scenario 4

For Scenario 4, both peak and mean ammonia concentrations are closely related to wind velocity. Figure 42 shows the predictions for an initial ammonia concentration in fly ash of 50 ppm with varying fresh air flow rates. As shown, peak concentration varied significantly under different fresh air flow rates. Under a higher ventilation rate, both peak and mean ammonia concentrations were much smaller.

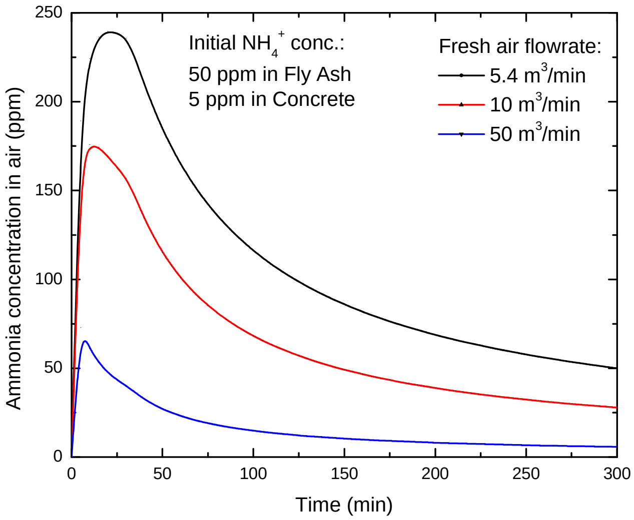

Figure 42: Predicted Ammonia Concentration Change with Time in Scenario 4

Different ventilation rates from 0 to 50 L/s per person (6 persons are involved) with three transportation/mixing times were then investigated. Figure 43 shows such predictions for Scenario 4 with comparison to 8-hr TWA of OSHA and NIOSH standards. If concrete is mixed inside the room, in order to follow both NIOSH and OSHA standards, ammonia concentration in fly ash should be less than 12.5 ppm if minimum ventilation rate of 7.5 L/s-person can be guaranteed. In a more common case, concrete usually is mixed in a mixing truck outside the room for at least 30 minutes. If so, ammonia concentration in fly ash of less than 55 ppm could satisfy the NIOSH standard.

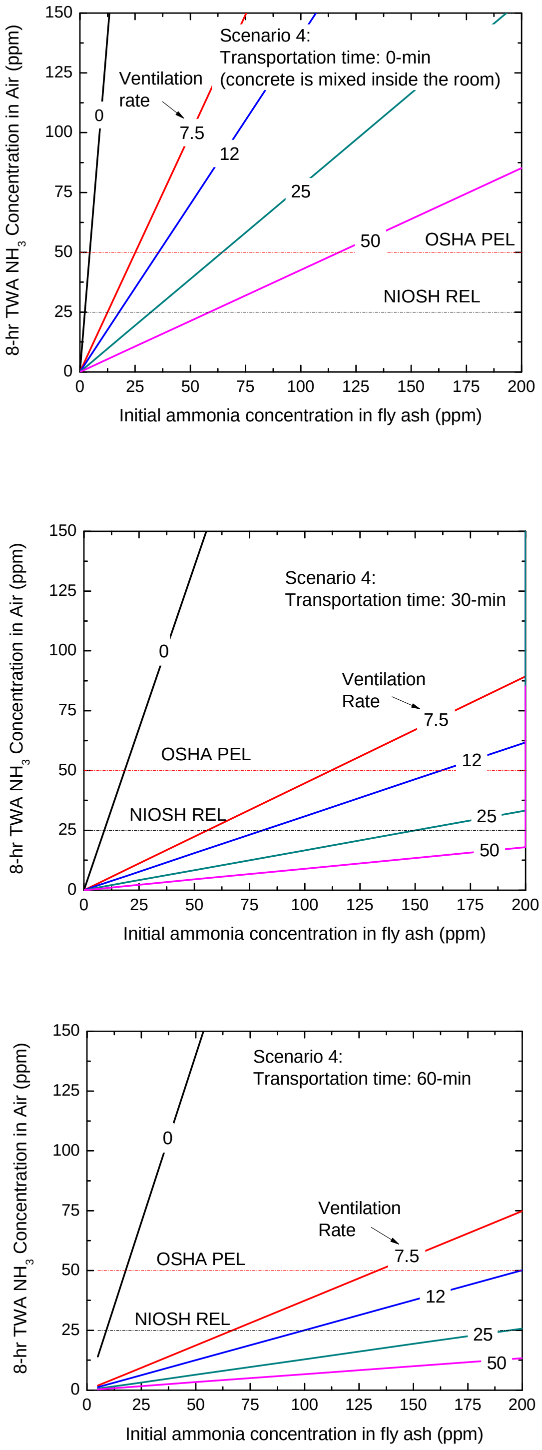

Figure 43: 8-hr TWA Ammonia Concentration as a Function of Initial Ammonia Concentration in Fly Ash with Various Ventilation Rates for Three Transportation/Mixing Times

10. Recommendations

According to the simulation results, for Scenario 1, ammonia usually can quickly diffuse to the ambient air and the concentration around the concrete slab is not expected to exceed OSHA, NIOSH or ACGIH exposure limits if ammonium concentration in fly ash can be kept lower than 100 ppm. In Scenario 2, if there is no dilution air and walls on both sides are very high, ammonia can be accumulated in the range of 3 m above the fresh concrete, which can be dangerous for workers who stay at the bottom of the form. However, in most common cases where the form is 5 to 7 feet deep, ammonia can be quickly diluted by wind at ground level and the situation will be similar with that in scenario 1. In Scenario 3, to avoid immediate high exposure to ammonia that can cause some health problems to workers, it is recommended that ammonium concentration in fly ash not exceed 50 ppm (5 ppm in concrete). If the lid is left open during driving, the ammonium concentration would be much lower. Otherwise, the driver/worker should absolutely avoid sticking his/her head into the headspace of the truck. In Scenario 4, if the minimum ventilation rate specified by ASHRAE of 7.5 L/s per person can be guaranteed and concrete is mixed outside the room for at least 30 minutes (the most common case), a threshold of ammonium concentration in fly ash of 55 ppm (5.5 ppm in concrete) is recommended in order to satisfy ACGIH TLV and NIOSH REL standards (25 ppm).

All above recommendations are based on laboratory-observed ammonia release rates and application of a semi-infinite diffusion model. It is possible that ammonia concentration can vary significantly in practice due to weather and the specific working environment. Therefore, field testing in scenarios where ammonia concentration is potentially high (e.g. at the bottom of a form, at the opening of a ready-mix truck, or just above the surface area of fresh concrete in the chute) can provide useful data in establishing the threshold for ammonium concentration in fly ash or concrete.

11. Summary and Conclusions

The research team was charged by the FDOT with providing recommendations for appropriate limits on the ammonia concentration in fly ash used as an admixture in concrete based on considerations including worker health and safety, chronic exposure concerns, nuisance odor problems, and concrete performance issues.

To meet this charge, the research team gathered information from the literature, the fly ash beneficiation industry, power companies that use coal as a fuel, the concrete industry, the cement industry, and government transportation department officials.

The research team evaluated the input from all of the parties named above and coupled this with an extensive set of laboratory experiments. The research team also developed a variety of exposure assessment models using assumptions that had been shared with the various industries named above. The conclusions below are the result of the feedback from the many parties who were contacted during this research project and the findings of the laboratory experiments and the exposure assessment modeling exercises.

Conclusions from this effort are as follows:

1. Industry and transportation department representatives commented in several cases that issues with ammonia (primarily odor complaints) were observed when concentrations of ammonia in fly ash were 100 ppm or greater.
2. One previous study examined potential worker exposure to ammonia as a result of ammoniated fly ash used as an admixture in concrete (University of Kentucky). That study recommended concentration limits of 240 – 375 mg NH_3/kg fly ash to meet the NIOSH recommended exposure level of 25 ppm in a scenario where little to no ventilation occurs and limits of 375 – 575 mg NH_3/kg fly ash when adequate ventilation occurs. It should be noted that the Kentucky study used a 20% fly-ash-to-concrete percentage as opposed to the 50% fly-ash-to-concrete used in the current FDOT study conducted by UF. The Kentucky study indicated that ammonia concentrations should be lower than 240 – 375 NH_3 mg/kg to prevent nuisance odor complaints by the persons placing (pouring) the concrete.
3. One state department of transportation, Missouri, indicated that they employed a rule of

thumb of 100 ppm as the maximum allowable concentration of ammonia in fly ash used for their concrete applications.

4. The only technology vendor currently operating systems in Florida for ash conditioning to reduce ammonia in fly ash indicated that their typical practice is to limit ammonia concentrations to less than 75 ppm in fly ash. This vendor operates ash conditioning systems at two power plants.
5. Laboratory chamber experiments found that ammonia release rates from concrete amended with ammoniated fly ash were greatest during mixing and pouring. The laboratory data indicates that the ammonia emission rate (from the concrete) decreased with time through the curing period. These laboratory results were used to determine mass transfer coefficients that were used in the exposure assessment modeling.
6. Although results varied as a function of input parameter selection, exposure assessment modeling for scenarios where concrete was poured in outdoor applications found that the NIOSH recommended exposure level in air of 25 ppm would not be exceeded under normal working conditions when ammonia concentrations in fly ash were less than 100 ppm.
7. Exposure assessment modeling for scenarios where concrete was poured in an indoor setting found that if a minimum ventilation rate was maintained, ammonia concentrations of 50 ppm in fly ash would not exceed the NIOSH recommended exposure level in air of 25 ppm. However, the exposure assessment modeling also found that under some scenarios (e.g., poorly ventilated environments such as one that might occur inside the drum of a mixing truck and at the bottom of a high-walled form with a continuous pour of concrete), ammonia concentrations to which a worker would be exposed could exceed safe levels even if ammonia concentrations in fly ash were less than 100 ppm. Please see the note below the conclusions regarding maintaining a safe workplace when concrete is being placed in a continuous pour “inside” a semi-confined space such as a pour with high walls surrounding the area where the concrete is being placed.
8. The leaching assessment of ammonia from hardened concrete samples made using ammoniated fly ash found that risk to public health or to the environment will not occur as a result of ammonia release from ammoniated concrete if fly ashes with an ammonia concentration less than 800 ppm are used.

9. The research team met with various representatives from the ash-conditioning industry over the course of the project on many occasions at several industrial facilities. The research team observed that various rapid "wet chemistry" techniques were used for measuring the ammonia concentration in ash at the industrial facilities. The industry representatives indicated that they are not sure if their field technique for measuring ammonia in fly ash gives results that are comparable to other test methods. There is a very clear and pressing need for the development of a simple standardized testing protocol that can be used by all of the parties involved in this industry (producers, conditioners and users of ammoniated fly ash) to quickly, accurately, and easily determine the ammonia concentration in the fly ash. Further research is needed to specify an ammonia assay which is accurate, rapid, and affordable.

Based on the above conclusions and the information presented in the report, the research team recommends that if FDOT chooses to specify an upper limit to the ammonia concentration in fly ash used for concrete production, 100 ppm would be protective of human health for most situations and would be achievable by vendors in the State of Florida using current ash treatment practices. The authors recommend, however, that under conditions where poor ventilation might occur, appropriate safety protocols should be evaluated by a trained professional (e.g., certified industrial hygienist) prior to job commencement so necessary safety measures and/or job-specific ammonia concentration limits are used. Job managers should also be aware that even with the utilization of a 100 ppm ammonia limit in fly ash, the occurrence of ammonia odors may not be eliminated.

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Appendix I – AFA Survey

The following survey was submitted to state transportation departments throughout the country. The results of the state survey are presented in Chapter 3.

AFA Survey

Are you directly responsible or aware of the processing, treating and approval of fly ash within your state agency? If so, please help us by answering the brief survey below. If not, we would greatly appreciate it if you would forward to the appropriate individual within your agency. The information requested is critical to our efforts here in Florida.

The Florida Department of Transportation is working with the Hinkley Center for Solid and Hazardous Waste Management and the University of Florida to investigate potential health and safety implications of ammonia concentrations in fly ash, cement, and concrete. As a result of the Clean Air Interstate Rule of 2005, coal-fired power plants have been utilizing air pollution control technologies that result in fly ash with elevated concentrations of ammonia (referred to herein as ammoniated fly ash, AFA). Uncertainty exists regarding the potential implications of AFA when used in transportation construction projects. Concerns of AFA use have been raised and science-based recommendations for appropriate limits based on considerations including worker health and safety, chronic exposure concerns, nuisance odor problems, and product performance issues are being studied.

Your response to the questions below will assist researchers with their review. A final report which will include the responses to this survey will be prepared and made available to those participating in this survey. We are grateful for your time and your commitment to the safety of our workers.

1. Is fly ash from the combustion of coal used in the production of cement or concrete in your state? (yes, no)
2. Is high ammonia in concrete (due to fly ash addition) a concern in your state?
3. Have you had complaints, issues, or questions about ammonia as it relates to concrete? If so, from what industries, or other sources?
4. Does your agency enforce or recommend any specifications regarding fly ash in cements or concrete? If so, please elaborate.
5. Does your agency enforce or recommend any specifications regarding ammonia in fly ash, cement, or concrete?
6. What actions (research, regulations, etc) in your state have been taken to address the ammoniated fly ash issue?

We would greatly appreciate the contact information of someone in your state who is experienced with these issues. Please list their information below:

Name ____

Agency ______________________________ **Title**____________________

Email ___________________________ **Phone** _______________________

Please return the survey to <u>center@hinkleycenter.org</u> by <u>Friday, July 22, 2011</u>.
Thank you for your time and interest!

Appendix II – Ammonia Emission Monitoring Methodology

This section provides a detailed description of the samplers associated with ammonia emissions monitoring in the glove box tests. The designs of experiments using these samplers are presented in Chapter 7 and the results are presented in Chapter 8.

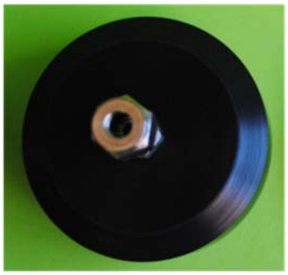
NIOSH Method 6016

- Sampler: Solid Sorbent Tube (sulfuric acid-treated silica gel): a 0.8 μm MCE prefilter may be used to remove particulate interferences
- Flow rate: 0.1 to 0.5 L/min
- Vol-min & max: 0.1 L & 96 L
- Accuracy: ± 14.5%
- Analyte: Ion Chromatography; ammonium ion (NH_4^+)

Figure 44: SKC Sorbent Tube

FIPR Personal Sampling System

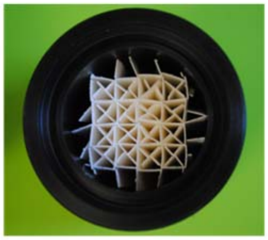
This new personal sampling device was developed by Dr. Wu's group. It consists of a parallel impactor, a porous membrane denuder (PMD) and a filter pack. In order to accurately access workers' exposure to inhaled dust, the impactor follows the entire ACGIH/CEN/ISOdefined respirable sampling convention. The denuder is used to remove gaseous compounds (ammonia in this case) while allowing fine aerosol to pass through the section. The last stage of the sampler, the filter pack, contains two filters to collect all the aerosols that pass through the impactor and the denuder. The results from the NIOSH 6016 sampler and the FIPR personal sampler provide a more accurate profile of aerosol and ammonia gas release during concrete mixing and curing period.


(b) Top cap (close faced)


(c) Top cap (open faced)


(e) Impactor top piece


(f) Impactor bottom piece


(g) Denuder

(h) Filter pack

Figure 45: FIPR Personal Sampling System

Honeywell PHD 6™ Gas Detector

The gas monitor used in the experiments is Honeywell PHD6™ Gas Detector equipped with a photoionization detection (PID) sensor to measure ammonia concentration from 0 to 3000 ppm. The body of the PID sensor is made up of a UV lamp, and an electrode stack. When the target gas enters the sensor's sensing chamber, the photons emitted from the UV lamp break up the molecule into two ions, one positively charged, one negatively charged. The electric field created by the anode and cathode in the stack attracts the ions, which results in an electric current. This current is then measured by the circuitry in the sensor and a signal is sent to the instrument, reporting the concentration.

Figure 46: Honeywell PHD 6^{TM} Gas Detector

Detection Range: 0/3000 ppm (standard)

Response Time:

T50 = less than 30 seconds

T90 = less than 60 seconds

Accuracy: +/- 5% of value, but dependent on calibration gas accuracy and time since last calibration