Development of a Standard Operating Procedure for Analysis of Ammonia Concentrations in Coal Fly Ash

FDOT Contract Number: BDV31-977-10

Final Report

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Disclaimer

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)				
ºF	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	ºC

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.
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16. Abstract

Research was performed to support the development and recommendation of a standard operating procedure (SOP) for analyzing the ammonia content in fly ash intended for use in concrete. A review of existing ash producers found that several different analytical approaches are currently in use. Preliminary research involved examining both ammonia extraction and analysis techniques. An assessment of accuracy, precision, cost, and test duration was conducted for three test methods (salicylate color disc, ion-selective electrode, and gas detection tubes). The research team is recommending a standard operating procedure (SOP) utilizing a methodology involving the use of gas detection tubes to measure the headspace concentration of liberated ammonia gas above a mixed fly ash slurry in a closed flask. The measured gas phase concentration of ammonia in the flask headspace is then related to the amount of ammonia in the fly ash which was sampled. This method was selected as a preferred procedure because of higher accuracy and precision, consistent results, appropriate test duration, ease of use, and practical running costs. This SOP was beta tested at an ash producing facility in central Florida, and the method was then refined to address facility operator comments.

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Executive Summary

Research was performed to support the development and recommendation of a standard operating procedure (SOP) for analyzing the ammonia content in fly ash intended for use in concrete. While the FDOT currently utilizes an ion–selective electrode (ISE) method to assay ammonia in samples at their research laboratories, the intent of this SOP was to set a standard for a more rapid technique for ammonia measurement at production level facilities (e.g., ash producers, concrete batch plants).

A review of existing ash producers found that several different analytical approaches are currently in use. Some rely on a colorimetric change in an aqueous solution, and others rely on reading a gas tube packed with a reactive indicating medium. Preliminary research involved examining both ammonia extraction and analysis techniques.

The research team is recommending an SOP utilizing a methodology involving the use of gas detection tubes to measure the headspace concentration of liberated ammonia gas above a mixed fly ash slurry in a closed flask. The measured gas phase concentration of ammonia in the flask headspace is then related to the amount of ammonia in the fly ash which was sampled. This method was selected as a preferred procedure because of higher accuracy and precision, consistent results, appropriate test duration, ease of use, and practical running costs. This SOP was beta tested at an ash producing facility in central Florida, and the method was then refined to address facility operator comments.

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Acronyms

AA – Acetic Acid

AFA – Ammoniated Fly Ash

CAA – Clean Air Act

CAIR – Clean Air Interstate Rule

DI – De-ionized

FCG – Florida Electric Power Coordinating Group

FDOT SMO – Florida Department of Transportation State Materials Office

IC – Ion Chromatography

ISE – Ion-Selective Electrode

L/S – Liquid-to-Solid Ratio

LNB – Low NO_x Burner

PCC – Portland Cement Concrete

QC – Quality Control

SCR – Selective Catalytic Reduction

SNCR – Selective Non-Catalytic Reduction

SOP – Standard Operating Procedure

ZHE – Zero Head Extraction

1. Introduction

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). Research conducted by the University of Florida and the Hinkley Center for Solid and Hazardous Waste Management on the potential risks associated with the use of AFA in FDOT projects reported that an ammonia concentration upper limit of 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 (Schert et al., 2012). The selection (and development as necessary) of a specific analysis technique for measuring ammonia in fly ash is then necessary as part of a safe ammonia level recommendation made by FDOT. The identification and development of an appropriate ammonia analysis technique should take into consideration both the cost and accuracy of test method as well how readily the method can be adopted and performed by end users with a broad range of skills and available resources.

The objectives of this project included conducting a detailed assessment of the current practices used for ammonia analysis in coal fly ash, necessary side-by-side laboratory testing of AFA samples using current methodologies, examining new analytical procedures, developing a draft SOP, conducting field tests of the SOP in cooperation with likely end-users, and finalizing the SOP based on the stakeholder and FDOT feedback.

2. Literature Review

2.1. Background

Coal fly ash is a by-product from burning pulverized coal in a boiler to produce electricity. It is captured from the plant exhaust gases by pollution control devices such as electrostatic precipitators, baghouse filters, and scrubbers. Fly ash is a very fine, particulate material mainly composed of silica with nearly all particles spherical in shape. Table 1 presents the composition of coal fly ash by source coal type (US EPA, 2011). It is also a pozzolan, a siliceous material which in the presence of water, will react with calcium hydroxide at ordinary temperatures to produce cementitious products. Because of its spherical shape and pozzolanic properties, fly ash is commonly used in cement and concrete applications. Its narrow particle size distribution also makes it a good mineral filler in hot mix asphalt applications improving the fluidity of flowable fill and grout when it is used for those applications. A list of common fly ash applications is presented below (US EPA, 2011):

- Raw material in concrete products and grout
- Feed stock in the production of cement
- Fill material for structural applications and embankments
- Ingredient in waste stabilization and/or solidification
- Component of flowable fill
- Component in road bases, sub-bases, and pavements
- Mineral filler in asphalt

Table 1. Composition by Percentage of Coal Fly Ashes by Coal Source

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

Researchers from the University of Florida and the Hinkley Center for Solid and Hazardous Waste Management recently completed (2012) an assessment of potential risks associated with the use of ammoniated fly ash (AFA) in FDOT projects. This research resulted in a recommendation that an ammonia concentration upper limit of 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 (Schert et al., 2012). This study's literature review and industry assessment found that no single common methodology is currently utilized, and that the techniques that might be amenable to analysis in the research laboratory might not be appropriate for analysis at the industrial facility or the concrete batch plant. The reader should consult the previous literature reviews in Schert et al. (2012) for a fundamental review of all aspects related to this issue. The literature review presented herein focuses on any additional scientific or industrial reports that have been published regarding this topic and specifically examines the analytical methodologies in the gathered literature.

2.2. Ammoniated Fly Ash Production and Use

In 2012, approximately 52 million tons of coal fly ash was produced in the United States and 12 million tons was used in the production of concrete and concrete products (ACAA, 2012). 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 while also reducing costs and increasing beneficial reuse (US DOT, 2011).

The Clean Air Act (CAA) Amendments of 1990 require large reductions in NOx emissions from coal-fired electric utility boilers. Furthermore, 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 composition of coal fly ash (FDEP, 2009; Kosson et al., 2009; Rathbone and Robl, 2001; Schert et al., 2012). In order to reduce NOx from flue gas emissions, selective catalytic reduction systems (SCR), selective non-catalytic reduction systems (SNCR), and low NOx burners (LNB) have been installed at many power plants to meet the CAA and CAIR standards. Each of these technologies may use ammonia as a reagent to lower NOx by forming molecular nitrogen and water. These pollution control systems can reduce NOx concentrations up to 50 percent (Brendel et al., 2000). However, unreacted injected ammonia is carried with the flue gases with a large part depositing onto the fly ash. It is generally believed that up to 80 percent of the ammonia slip from SCR is adsorbed on the fly ash (Brendel et al., 2000).

The increased ammonia concentration has raised concerns regarding the health of workers using cement/concrete amended with ammoniated fly ash.

2.3. Existing Studies on Ammoniated Fly Ash (AFA)

Existing literature on AFA has been gathered and examined as presented in Table 2. Research conducted by Wang et al. (2002) evaluated ammonia release characteristics from AFA by using a sequential batch leaching procedure on AFA samples using DI water, followed by analysis using ammonia ion-selective electrode (ISE). Palumbo et al. (2007) characterized AFA by extracting ammonia with 2M KCl solution in a shaker and analyzing the extractant by automated colorimetry. Mehta et al. (2004) characterized AFA, as described in a patent by first extracting ammonia with 2% v/v % H_2SO_4 mixed with DI water in an ultrasonic bath, followed by analysis using an ISE, although it was noted that potassium was a known interference. In the research conducted by Brendel et al. (2000), ammonia was extracted using DI water and agitation, and the filtrate was analyzed by an ISE. It was also reported that due to interferences caused by other monovalent cations in solution, the measured NH_4^+ concentrations were higher than the actual concentrations, particularly at lower NH_4^+ levels (i.e., <20-25 ppm) (Brendel et al., 2000). Cardone et al. (2005) conducted a column test on AFA samples by using a liquid chromatography column and DI water. The eluent was analyzed using an ISE after adjusting the pH to >12 (Cardone et al., 2005). Wang et al. (2007) characterized AFA samples by conducting a batch leaching test under varying pH conditions. Nitric acid and sodium hydroxide were used to adjust pH of leaching solutions. The leachate was analyzed using the Hach Method (Salicylate Method). Under the conditions of this study, it was found that pH did not impact the leachate ammonia concentration, indicating both NH_3 and NH_4^+ are highly soluble (Wang et al., 2007).

Electric Power Research Institute (EPRI) conducted a series of studies related to ammonia and AFA (Golden, 2001; Ban, 2001; Hinton et al., 2002; Cannon and Cushing, 2005). Of the four studies reviewed, one focused on the leaching of ammonia from AFA (Ban, 2001). Ban (2001) identified the issue that there are no standard or generally accepted procedures for fly ash ammonia leaching. He established leaching procedures based on existing testing procedure for solid waste leaching. Batch, serial batch, and column leaching were conducted to simulate various conditions (Ban, 2001). Ammonia extraction effectiveness was evaluated by varying factors such as extraction solution (DI water or 0.1 M acetic acid), time, and agitation. ISE was employed to analyze ammonia concentration in the leachate (Ban, 2001).

Identifying a specific analytical method for ammonia analysis is an important aspect of any materials specification that FDOT makes. Extensive literature review and an industry assessment found that no single common methodology is currently utilized, and that the techniques that might be amenable to analysis in the research laboratory might not be optimal for analysis at the industrial facility or at the concrete batch plant. Thus, FDOT has sponsored this project to identify (and develop as necessary) a methodology that both provides an accurate measurement of ammonia concentrations in coal fly and that can be readily and economically performed by end users with broad ranges of capability and resources.

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

Name	Institute/Company	Research
Timothy G. Townsend	University of Florida	Leaching
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
Stephen Gasiorowski	Titan Cement Group	Removal
Indrek Kulaots	Brown University	Adsorption mechanism
Brendel	GAI Consultant, Inc.	Characterization and leaching
Various	Electric Power Research Institute	Characterization and leaching

2.4. Ammonia Analytical Techniques

2.4.1. Ammonia Chemistry

In order to understand ammonia analytical techniques it is important to understand some basic ammonia chemistry. Ammonia is a colorless, polar, toxic gas that is highly soluble in water (Brendel et al., 2000):

$$NH_{3(g)} + nH_2O_{(l)} \leftrightharpoons NH_3 \cdot nH_2O_{(aq)} \qquad (1)$$

Aqueous ammonia is a weak base since hydroxide and ammonium ions will be released into solution upon dissociation. Aqueous ammonia nitrogen is present in two forms: un-ionized NH_3 and ionized NH_4^+. Un-ionized NH_3 is highly toxic to aquatic organisms whereas NH_4^+ is much less so (Thurston et al., 1977). The relationship between the two species can be expressed as a chemical equilibrium (Brendel et al., 2000):

$$NH_3 \cdot nH_2O_{(aq)} \leftrightharpoons NH_4^+ + OH^- + (n-1)H_2O_{(l)} \qquad (2)$$

The relative abundance of these two species are primarily dependent on the pH of the solution, and temperature to a lesser extent. Figure 1 presents the effect of pH on the equilibrium ammonia species distribution in water at 25°C. The fraction of unionized NH_3 increases as the pH increases. At a pH of approximately 9.2 (pKa), the equilibrium concentrations of un-ionized NH_3 and NH_4^+ ion are equal. Increased temperature shifts the curves to the left (lower pH), whereas decreased temperature shifts the curves to the right (higher pH).

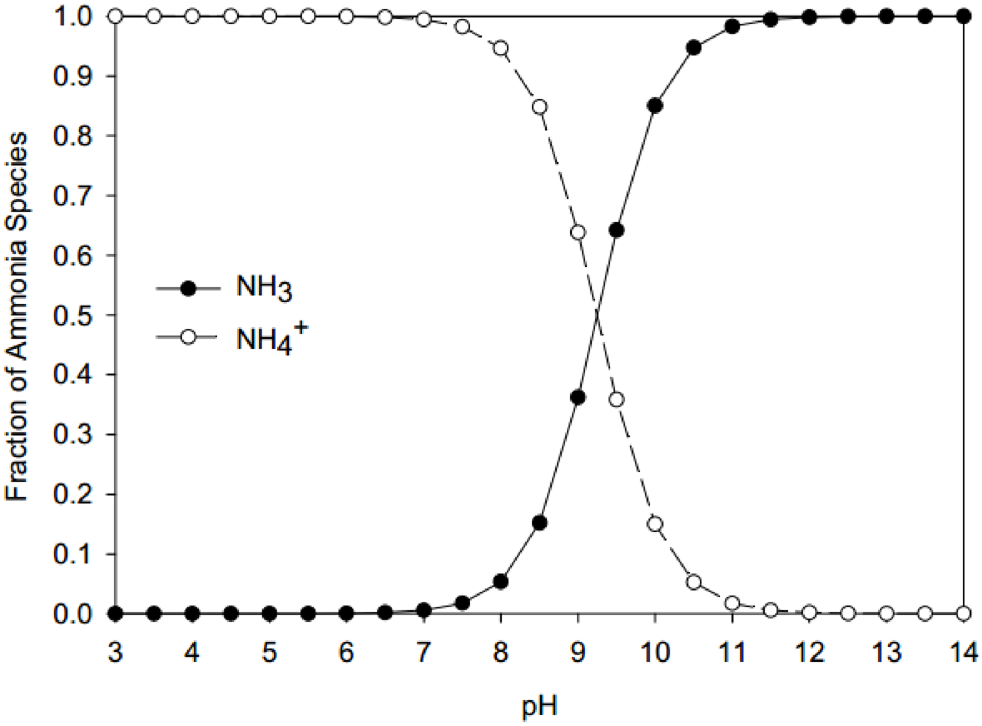

Figure 1. Ammonia species in aqueous solution as a function of pH at 25 degrees Celsius (Emerson et al., 1975)

Besides pH and temperature, salinity (ionic strength) can also exert an influence on ammonia solubility as well as on the species distribution (Bower and Bidwell, 1978). Figure 2 presents the effects of salinity on percent un-ionized ammonia in seawater at 25°C. Increased salinity (ionic strength) causes decrease in % un-ionized ammonia.

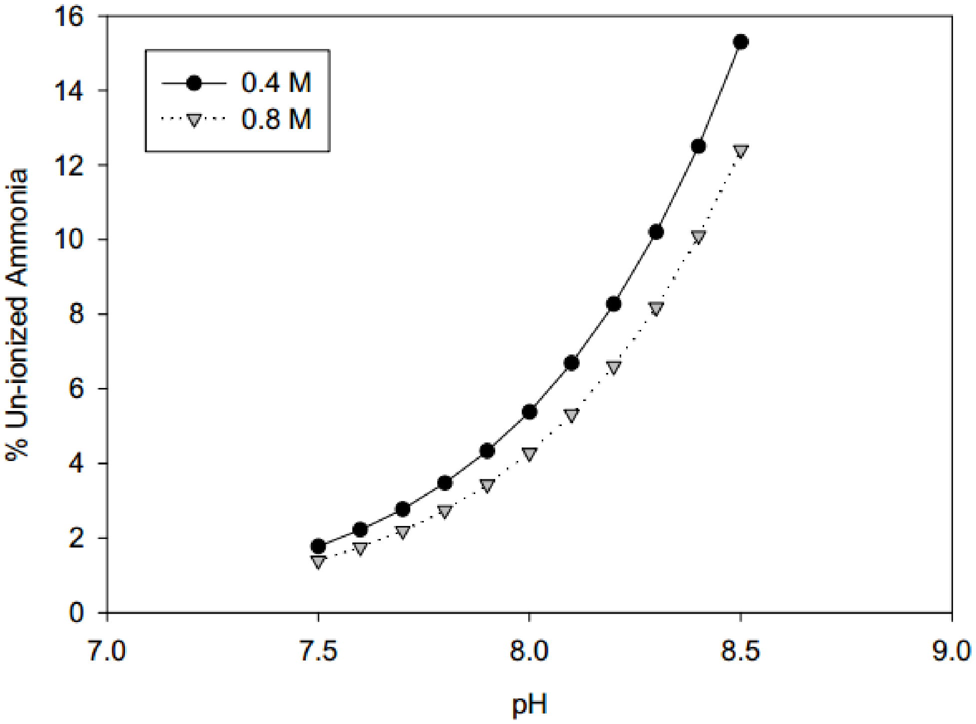

Figure 2. Effect of salinity (ionic strength) on the percent of un-ionized NH_3 in aqueous solution at 25 degree Celsius (Bower and Bidwell, 1978)

2.4.2. Ammonia Extraction Techniques

It is known from the literature that ammonia in the flue gas can be deposited on the fly ash as highly soluble salts ammonium bisulfate and ammonium sulfate when sulfur is present in the flue gas (Cushing and Hinton, 2004; Golden, 2001; Hinton et al., 2002; Wang et al., 2002). Additionally it was found that there was no significant difference between the leaching behaviors of these two salts. In the study conducted by Wang et al. (2002), 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 by 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 are highly soluble and can be readily leached from the fly ash surface by “washing” with deionized water (Hayes, 2013). The most common method for extracting ammonia from AFA uses DI water in combination with agitations by shaker or rotators (Cardone et al., 2005; Cushing and Hinton, 2004; Brendel et al., 2000; Golden, 2001; Hinton et al., 2002; Wang et al., 2002). KCl extraction technique was found in only one AFA study in combination with colorimetry analysis (Palumbo et al., 2007), despite the fact that KCl is the universal extractant for soil analysis (Li et al., 2006). KCl was found to be less favorable than DI water in extracting ammonia from AFA largely due to its interference with the popular ISE analytical technique (Brendel et al., 2000; Mehta et al., 2004). Another study used 2% v/v % H_2SO_4 mixed with DI water to extract ammonia from AFA (Mehta et al., 2004). Ammonia in AFA was converted to ammonium sulfate, which is the most common form of ammonia in AFA, and was dissolved in DI water.

The study conducted at EPRI by Ban (2001) concluded that sample pH in 10:1 L/S ratio varied significantly. Agitation did not significantly affect ammonia leaching although it affected the pH (Ban, 2001). Extraction using DI water and 0.1 M acetic acid did not produce a significant difference in ammonia leaching, and the release rate was similar (Ban, 2001). Most of the ammonia, about 70% - 80%, was released in the first 10-30 minutes, depending on the sample (Ban, 2001).

Available literature regarding analysis of ammonia concentration in other matrices (e.g., soil, sludge, and other types of wastes) were compiled. The universal soil extractant was found to be 1-2 M KCl. It is commonly used for nitrogen extraction in combination with colorimetry analysis (Keeney and Nelson, 1982; Kempers and Zweers, 1986; Knepel, 2003; Li et al., 2006; Switala, 1993; Tel and Heseltine, 1990). One study extracted ammonia from silage samples by also using 2 M KCl solutions (Kozloski et al., 2006). An alternative soil extraction method was proposed replacing 2 M KCl with 0.2 M $SrCl_2$, however it concluded that $SrCl_2$ did not perform well in soil with high calcium carbonate (Li et al., 2006). Ammonia analysis in drinking water, groundwater, surface water, and in domestic and industrial waste and biosolids is specified by EPA Method 1689. In Method 1689, ammonia is extracted by distillation to eliminate potential interferences then analyzed using ISE.

2.4.3. Ammonia Analysis Techniques

A series of standard ammonia extraction and analysis methods has been compiled and presented in Table 3 below.

Table 3. Ammonia Collection and Analysis Methods

Method Number	Method Title
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

A number of analytical methods are available for measurement of ammonia on AFA. Two major factors that influence selection of the method to determine ammonia are concentration ranges and the presence of interferences. The majority of these techniques rely on the extraction of ammonia from the AFA and subsequent determination of total ammonia in the extracting solutions. Seven common methods were identified:

- Nesslerization Method
- Titrimetric Method
- Phenate Method
- Ion-Selective Electrode
- Ion Chromatography

- Salicylate Method

2.4.3.1 Nesslerization Method

Aqueous samples are carried through the process of Nesslerization. The absorbance or transmittance of samples is measured and results are determined from a calibration curve of known standards. The detection limit for this method is approximately 0.4 μg/mL. However, this method has been dropped as a standard method, even though it has been considered a classic water quality measurement for more than a century. The use of mercury in this test warrants its deletion because of the disposal problems (Eaton and Franson, 2012).

2.4.3.2 Titrimetric Method

This method is used only on samples that have been carried through preliminary distillation. Aqueous samples are mixed with an indicator (boric acid solution) and titrated with 0.02 N sulfuric acid until the indicator color change (turns a pale lavender). The concentration of ammonia will then be calculated using the amount of sulfuric acid added and the sample mass. The detection limit for this method is approximately 5.0 μg/mL (Eaton and Franson, 2012). However this method has two major drawbacks: distillation is time-consuming; and the equipment required is expensive (Adepetu et al., 1996).

2.4.3.3 Phenate Method

Aqueous samples are treated with various reagents to form a blue color. The absorbance is measured by a spectrophotometer, and the results are determined from a calibration curve of known standards. The detection limit for this method is approximately 0.2 μg/mL (Eaton and Franson, 2012). Note that ASTM has discontinued the use of the automated colorimetric phenate method (Hinton et al., 2002).

2.4.3.4 Ion-Selective Electrode (ISE)

Response of known standards is made using an ammonia-ion-specific electrode and a voltmeter. This defines the calibration curve. The aqueous samples are measured, and values are referenced on the calibration curve (Hinton et al., 2002). This method is applicable to the measurement of

0.03 to 1400 mg NH_3-N/L. (Eaton and Franson, 2012). The ammonia electrode method is fast gaining popularity as a rapid and inexpensive method for N determination. The electrode is much like a pH electrode, but measures the concentration of ammonia in solution (Adepetu et al., 1996). Interferences can be caused by monovalent cations in solution (Brendel et al., 2000).

2.4.3.5 Ion Chromatography (IC)

Samples are analyzed on an ion chromatograph set up for cation analysis. The ammonium (NH_4^+) concentration of the sample is used to determine the ammonia concentration. The detection limit for this method is approximately 1.0 µg/mL and the applicable range is 0.05–40 mg/L. Generally, instrument specific methods must be developed for this technique (Hinton et al., 2002).

2.4.3.6 Salicylate Method

The salicylate method for ammonia analysis was introduced in early 1980s as a substitute for the toxic phenol method (formation of volatile ortho-chlorophenol) (Kempers and Zweers, 1986). Reagents are added into the aqueous solution to develop color. The absorbance is measured with colorimetry and the concentration can be determined from the calibration curve. This method is most useful for low range ammonia nitrogen determinations.

2.5. Comparison of Methods

All of the methods mentioned above have reasonably good replicability and appear to compare favorably with each other. To determine which method to use for ammonia analysis depends on factors such as ammonia concentration, temperature, chemical interferences, ease of operation, analysis time, cost of reagents and supplies, and cost of instrument, which is associated with detection limits and errors while interpreting the results. For example, a commercial lab that performs many analyses might prefer to use IC, for precision and replicability, while ISE might be the favorable choice for field testing, because of speed, cost, and simplicity (Hinton et al., 2002).

Currently the most commonly used methods are ISE and IC (Hinton et al., 2002). ISE is used for quick determination followed by confirmation with IC. ISE requires little initial investment and it seems to produce reproducible and accurate results. ISE and IC are the preferred method for many operating plants and no particular interferences with either of the two methods were found on measuring ammonia from AFA (Hinton et al., 2002).

3. End-User Survey

3.1. Introduction

This section of the report describes the outcomes of the Task 2 - End-User Survey. Potential end users of an SOP were surveyed to assess (i) what methods they use or know of, (ii) what are the primary needs and concerns they would have in functional SOP, (iii) what interest they might have in testing any draft SOPs, and (iv) what is their technical background/skill set. This report for Task 2 will present a summary of standard methods as well as specific methods identified from surveying those stakeholders we contacted.

3.2. Potential End Users

To fulfill Task 2, it was necessary to identify those facilities where ammonia assays on ammoniated fly ash were being practiced. The researchers contacted both Florida Department of Transportation State Materials Office (FDOT SMO) and the Florida Electric Power Coordinating Group (FCG), and performed internet searches for sites where ammoniated fly ash (AFA) would likely be managed. We also contacted out of state companies for the same information. People contacted for information and or survey questions are presented in Table 4.

Table 4. Identified Potential End-Users

Contact Name	Organization Name
Mike Bergin	FDOT SMO
Toby Dillow	FDOT
Mike Petrovich	Florida Electric Coordinating Group
Robert Stafford	Duke Energy
Justin Gosnell	Seminole Electric
Rafic Minkara	Headwaters Resources
Jorge Tercero	Separation Technologies
Kirk Elison	Southern Companies
Craig Wallace	Headwaters Resources

3.3. Analysis Methods Identified among the Industries

3.3.1. Direct Nesslerization (Used by Separation Technologies)

The Separation Technologies laboratory facility at Tampa Electric Company (TECO) Big Bend power plant currently uses a process called direct nesslerization to measure the ammonia content of the fly ash treated at this facility. It allows fast, low-cost and easy-to-operate determination of ammonia in the field. However, it has limited resolution, and its accuracy and reliability compared to standard methods is unknown.

A small sample of fly ash is removed from the separator and analyzed using direct nesslerization every 30 minutes. The actual size of the sample used in the analysis is quite small, approximately 5 grams, and the method is performed rapidly, in less than 5 minutes.

After the sample to be analyzed is weighed out, a small volume of water (10 mL) is added to the sample and it is vigorously shaken. The sample is filtered through a 0.45-µm membrane filter. The pH is adjusted to 10.5 with NaOH to precipitate Ca, Mg, Fe, and sulfides and the sample is again mixed. Next, Nessler's reagent (100 g HgI_2 + 70 g KI dissolved in water added slowly to a cool solution of 160 g NaOH in 500 mL water and diluted to 1.00 L) is added and mixed by inverting the Nessler tube. To determine ammonia concentration the sample is visually compared to the color chart developed with standards.

3.3.2. Measuring Ammonia Concentration in AFA by Gas Sampling Tubes (Used by Headwaters Resources)

A derivative of this method is used by Headwaters Resources who handles the assay for ash management within the Southern Company. Headwaters is one of the nation's leading ash suppliers.

A sample of fly ash and a measured amount of water is added to a clean 1 L Erlenmeyer flask with a stir bar. After mixing for one minute, an aliquot of aqueous sodium hydroxide is added to bring the pH above 12. The flask is immediately stoppered with a 2-hole stopper which was previously fitted with an ammonia detector tube and a manual gas sampling pump (specific for the brand of tube used). After a short stirring period, the headspace gas is measured by actuation of the pump and reading ammonia concentration result on the tube. A multiplier is applied to the result based on a standard curve.

3.4. Standard Analysis Methods Identified

3.4.1. Ammonia Concentration in AFA by Ion Chromatography (IC)

As a contrast to the simpler onsite methods used by the industry, typical laboratory methods of determining ammonia concentration in analytical labs are described below. A sample of fly ash is weighed out to 40 grams and placed inside of a Zero Headspace Extractor (ZHE). The purpose of a ZHE is to exclude any headspace for volatile constituents to volatilize into during the extraction procedures. Next, a syringe is attached to the ZHE and 500 mL of DI water (18.2 MΩ-cm) is pulled into the ZHE. The mixture is then agitated (in an end-over-end fashion) for one hour. After one hour, a syringe is again connected to the ZHE and 375 mL of the fluid is pulled out of the ZHE. The fluid is filtered by 0.45 µm borosilicate glass fiber filters housed within the ZHE. The 375 mL extraction is acidified to pH < 2 by adding 1 mL of concentrated HCl; the sample is stored at 4˚C until ion chromatography can be performed.

After the 375 mL sample has been extracted, an additional 375 mL of ammonia free DI water is added back to the ZHE and it is again agitated for one hour. After one hour, another extraction of 375 mL is pulled from the ZHE and stored for IC (ion chromatography) analysis. As before, the 375 mL extraction is replaced with clean DI water and a final extraction is performed after another agitation period.

The purpose of this extraction procedure is to dissolve all ammonium sulfate (the predominant ammonium salt which is found in the ammoniated fly ash samples) adsorbed to the fly ash into the extraction fluid. By acidifying the sample below a pH of 2, all the ammonia in the sample is converted to ammonium. Ammonium is an ion and its concentration can be determined by IC analysis. Knowing the liquid, to solid ratio used in the extraction and the concentration in the extraction fluid the concentration of ammonia (as ammonium sulfate) adsorbed to the fly ash sample can be determined.

When samples are ready for analysis using the IC, samples are simply loaded into an auto-sampler and analyzed by the Dionex Ion Chromatograph. The principle behind IC is the separation of constituents according to their differing transit time through a packed column. Based on the retention time of the analyte and its peak area the analyte can be identified and its concentration determined by comparison to standard concentration chromatograms. Below is an example of an IC chromatogram:

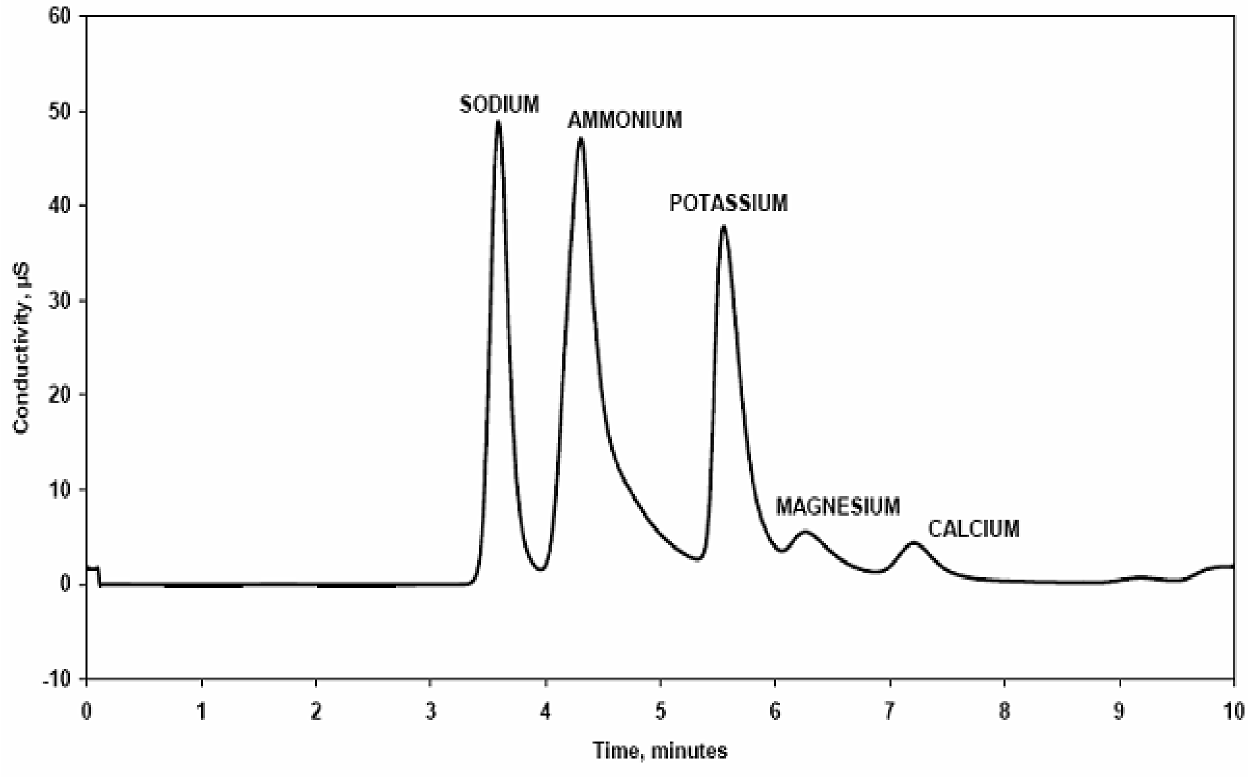

Figure 3. Example of an IC chromatogram

3.4.2. Measuring Ammonia Concentration in AFA by Ion-Selective Electrode (ISE)

Ammonia is extracted from AFA using similar methods described in section 4.1 followed by analysis using ammonia ISE. ISE allows fast, simple, economical, and accurate measurements of dissolved ammonia in aqueous solutions. It uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. Ammonia diffusing through the membrane dissolves in the ISE filling solution and the electrode will measure the electric potential. The electrode potential measured by the ISE is proportional to the ammonia concentration in the sample.

3.5.Primary Needs and Concerns for a Functional SOP

Based on the survey results, two primary needs and concerns were identified:

a) “Low initial costs of equipment, relatively quick, reliable and verifiable, low cost of supplies.”

b) Standardized method so that all suppliers were providing specification of ash based on the same assay.

3.6. Parties Interested in Participating in Testing Draft SOP

Two facilities were found to be interested in testing a draft SOP developed in this study:

1. Headwaters
2. Separation Technologies

3.7. Assays in the Field

The technicians found that personnel performing the ammonia assays in the field (respondents from Headwaters and site visit with Separation Technologies) were not chemists but had years of experience working with fly ash and had been trained in the specific assay in place and on the equipment needed to perform it.

According to some of the potential end users, some specific responses were not applicable so the verbatim responses are shown below:

Seminole Electric: “Our facility does have ammoniated fly ash but does not perform the testing ourselves. Instead we send our samples out to a contract laboratory. The specific laboratory changes as we re-bid the contracts whenever they expire. The method that is used by the lab is EPA 350.1M. We are interested in knowing how much ammonia we are dealing with in fly ash but since we do not perform our own testing, would not be useful in developing an SOP.” Duke Energy: “At one time, we generated elevated ammoniated fly ash as a result of an air pollution control system. That ash as I understand it eventually was beneficially used but not in FDOT related projects. We no longer produced ammoniated fly ash as the air pollution control system was changed to hydrated lime injection thus, eliminated ammoniated ash production.”

3.8. Summary

There were fewer facilities found performing their own ammonia assays than expected. Besides the commercial lab, only two methods were identified:

a). Colorimetric using Nessler's reagent

b). Gas sampling tubes to measure evolved NH_3 in headspace after raising pH.

Of the methods found in use, the order of expected costs (we did not receive cost for commercial labs) from highest to lowest ranks as: Commercial Labs, Gas Sampling Tubes, Nessler's reagent.

The information found in Task 2 will be used to guide the selection of a series of analytical methods to be evaluated in Task 4 in order to propose an effective and cost efficient SOP.

4. Ammonia Extraction Technique Assessment

This section of the report describes the investigation to determine the optimal extraction technique for the transfer of ammonia from the solid phase ammoniated fly ash (AFA) into the liquid phase (the extract), which will be needed for most analytical techniques. Sequential extractions and batch leaching tests were conducted to evaluate the influence of a variety of extraction parameters on extraction efficiency. These factors included: liquid-to-solid ratio (L/S), extraction solution, extraction time, degree of agitation, sample processing, chemicals used, and cost. Actual AFA samples were used for method development, and coal fly ash spiked with ammonium sulfate salts was used as a quality control (QC) measure.

4.1. Determining an Optimal Extraction Technique

The extraction of ammonia from coal fly ash was tested using two different methods: batch leaching test and sequential extraction. The batch leaching test was used to determine the extent of ammonia leaching under a given set of conditions. The AFA sample and extraction solution were mixed, and a measurement was taken after a certain time period to determine the ammonia concentration in the extract. Results from the batch leaching test provided insights on the influence of the different leaching parameters on the extent of ammonia leaching from AFA. A sequential extraction technique was used to determine the total ammonia content contained in the AFA. It involved repeated leaching of the same AFA sample with leaching fluid renewed at scheduled intervals. The experimental apparatus, chemicals used, procedures, and fly ash samples are described below in detail.

4.2. Experimental Apparatus and Chemicals Used

4.2.1. Apparatus

As previously discussed in the Task 1 report, the relative abundance of un-ionized (dissolved) ammonia (NH_3) and ammonium ion (NH_4^+) is primarily dependent on the pH of the solution and, to a lesser extent, on the temperature and ionic strength. A significant amount of NH_3 will be present in the liquid phase at pH > 7. In such a scenario, a zero-head-space extractor (ZHE) would need to be used to prevent possible ammonia loss when the liquid is in contact with air. Due to the large number of tests required in this study, syringes (BD 60 mL Syringe with Luer-Lok Tips) were used as a simple, rapid, and economic alternative to the ZHE, as shown in Figure 4. Threaded syringe tip caps were screwed onto the Luer-Lok syringe tips to prevent ammonia loss during the extraction. Syringe filters (Fisherbrand 0.45µm Nylon Syringe Filter 09-719-007) were used to filter the extract prior to the analysis. A comparison between the ZHE and the hypodermic syringe can be seen in Figure 4 (Ban, 2001). Hypodermic syringes were used in both batch leaching test and sequential extraction. When the extract pH is less than 7 with the use of acidic extraction solutions, a 60 mL glass beaker or a 50 mL centrifuge tube was used in some of the batch leaching tests.

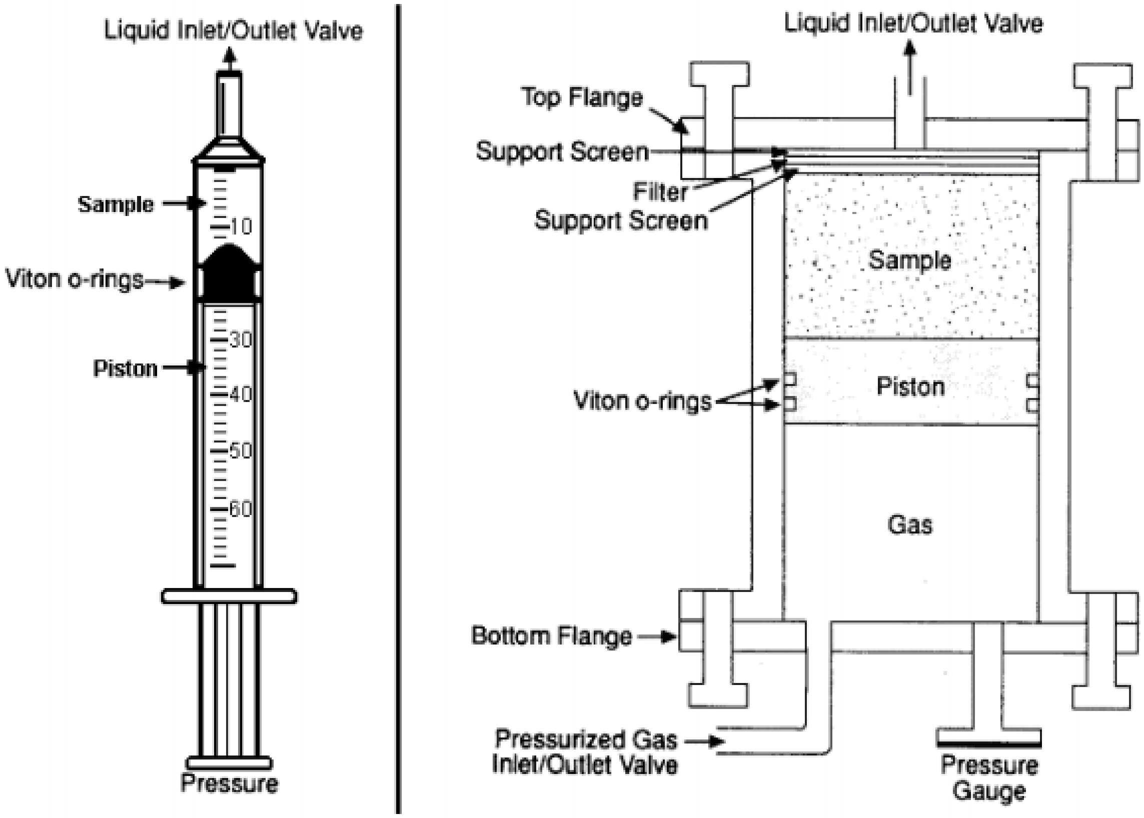

Figure 4. Comparison of a ZHE (on left) and its alternative, a hypodermic syringe (on right) (syringe filter not shown) (Ban, 2001)

4.3. Analytical Instrumentation

An ammonia ion-selective electrode (ISE) is a commonly used instrument for determining the concentration of ammonia in fly ash. ASTM D1426 uses ISE to test the ammonia content in water, and the ISE was included in the project scope as a baseline comparison method. The ISE allows fast, simple, economical and accurate measurements of dissolved ammonia in aqueous solutions. Although the ISE analysis method was selected for extraction method development, other analysis methods will be evaluated and discussed in Task 4. A Thermo Scientific Orion ISE (9512HPBNWP) was used to measure ammonia concentration in the extract for all experiments conducted in Task 3. The ammonia ISE uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. Ammonia diffusing through the membrane dissolves into the ISE filling solution. The filling solution contains ammonium chloride, and the electrode will measure the electric potential of the filling solution. The electrode potential measured by the ISE is proportional to the ammonia concentration in the sample (Thermo Scientific, 2007)

Measurements were taken in accordance with the procedure specified in the High Performance Ammonia Ion-Selective Electrode User Guide (Thermo Scientific, 2007). A four-point calibration curve that brackets the extract ammonia concentration was made every time right before taking the measurement using freshly prepared standards. The standards were made by diluting the 1000 ppm NH_3 standard in volumetric flasks using DI water. After the extraction, 20 mL of sample was transferred from the extraction apparatus to a small 60-mL beaker. And then, 0.4 mL of Ionic Strength Adjuster (ISA) was added immediately. Measurements were taken when the electrode readings were stabilized while the samples were being stirred by a magnetic stir bar at a moderate and constant speed. The whole measurement process was able to be completed within 1 minute per sample therefore the error caused by ammonia gas escape during the measurement was minimized.

4.4. Chemicals Used

Deionized water (DI) was used for all analyses and preparation. Ammonia standard solution (Orion ISE 1000 ppm Ammonia Calibration Standard) was purchased from Thermo Fisher Scientific and was used to make ISE calibration standards throughout the study. Orion pH Adjusting Ionic Strength Adjuster (ISA) (Cat. No. 951211), for samples that had a concentration of 1 ppm or higher as nitrogen, and Alkaline Reagent (low level ISA) (Cat. No. 951011), for samples that have a concentration of 1 ppm as nitrogen or lower, were also purchased from Thermo Fisher Scientific. ISA provides a constant background ionic strength and adjusts the solution pH to higher than pH 12, with pH indicating blue dye for instant verification. The use of ISA raises the solution pH to convert ammonium ion in the solution to ammonia gas, therefore allowing it to be detected by the ISE. In addition, ISA can also remove interferences from metallic ions by precipitating metals at high pH (Thermo Scientific, 2007). Orion pH 4, 7, 10, and 12 standard buffer solutions were purchased from Thermo Fisher Scientific for pH meter calibration. Hydrochloric acid and acetic acid (Fisher Brand Certified ACS Plus) was used for preparing ammonia extraction solutions and were purchased from Thermo Fisher Scientific. Potassium chloride (Fisher Brand USP/FCC Crystalline) was used to prepare ammonia extraction solution. Ammonium Sulfate (Fisher Certified ACS Granular) was used to spike coal fly ash (FA) to the predetermined concentrations. The spiked sample preparation will be discussed later in the text.

4.5. Sample Collection and Characterization

The AFA samples used were the same samples collected in the previous study (Schert et al., 2012), which were supplied by the Crystal River Power Complex located in Crystal River, FL. Additional fly ash (FA) samples with no ammonia were also collected from Gainesville Regional Utility located in Gainesville, FL. They were later spiked with ammonium sulfate salts to create two samples with known ammonia concentrations. All samples were stored in sealed borosilicate glass jars with minimal headspace. A total of four samples were used in this study, including two AFA samples (AFA-High and AFA-Low) and two spiked FA samples (FA-High, FA-Low). The samples were selected and prepared in an attempt to cover a wide range of ammonia concentrations in AFA that can be generated by the industry due to the use of NOx control devices such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).

All samples were analyzed for moisture content, natural pH, and original ammonia content as an initial characterization. There is no standard or commonly accepted methodology for ammonia extraction from coal fly ash. The methodologies used for characterizing AFA and FA samples were established based on appropriate methods identified from a literature review and procedures for solid waste leaching.

Moisture content was measured in triplicate following American Society of Testing and Materials method ASTM D2216 and verified throughout the course of the experiments (American Society of Testing and Materials, 2010). The moisture content of the sample was determined by placing 5-10 grams of FA or AFA into an alumina crucible and heating the samples at a constant temperature of 105 ± 20 °C for 24 hours in an oven (Thermo Fisher IsoTemp). Samples were then cooled to room temperature in a desiccator for fifteen minute and before the dried masses were recorded. Natural pH of the FA and AFA samples were taken in triplicate after immersing each sample in DI water for 24 hours at L/S = 10:1. Table 5 presents the average moisture content and pH of each sample.

Table 5. Moisture Content and Natural pH of AFA and FA Samples

Sample Identification	Natural pH	Moisture Content (%)
AFA-High	11.15	0.31
AFA-Low	11.49	0.31
FA	10.09	12.0

The moisture contents for both AFA-High and AFA-Low were found to be at very low levels (0.31%). Therefore, ammonia volatilization from AFA was unlikely. However, FA sample had a moisture content of 12.0% which could result in ammonia volatilization under high pH conditions. FA sample was intended to be spiked with ammonium sulfate salt to create samples with known ammonia concentration; it was important to prevent ammonia loss from the spiked samples. Hence, FA sample used for creating spiked samples were oven dried at 105 ± 20°C for 24 hours until the moisture content was measured at 0.01%. After drying, FA samples and ammonium sulfate salt were mixed to create spiked FA samples at 1000 mg-NH_3/kg-FA (FA-High) and 100 mg-NH_3/kg-FA (FA-Low) based on mass balance calculations. FA samples and ammonium sulfate salts were placed in two 2-L Teflon bottles and rotated on a rotator to mix for 72 hours to ensure homogeneity, as shown in Figure 5.

Figure 5. Mixing FA and ammonium sulfate salt on a rotator to create spiked FA samples.

To measure the ammonia content of each sample, a syringe was used for sequential extractions of fly ash samples using DI water at a L/S ratio of 10:1. In each test, 5 g samples of AFA or FA were weighted to 0.001 g and placed in a 60-mL plastic syringe. Then 50 mL of DI water was drawn into another syringe before it was injected into the sample syringes by using a syringe connector. No headspace was observed during the fluid transfer process. The syringes were sealed with syringe tip caps to prevent the ammonia escape. All syringes were rotated on a rotator at 1 hour interval. At the end of each interval, 30 mL of the extract was replaced with 30 mL of fresh DI. From the 30 mL of the extract, 10 mL of the extract was used for pH measurement and 20 mL of the extract was immediately measured for ammonia concentration using the ISE. This process was repeated until no ammonia was detected in the extract. The corresponding ammonium concentration of the extracted fluid was used to directly calculate the ammonium concentration adsorbed to the fly ash sample as follows:

$$\mathrm{C_{AFA,Total}} = \mathrm{C_{IC,i}}\left[\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right] + \left[\mathrm{C_{IC,i+1}}\left(\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right) - \frac{\mathrm{M_{AFA,i}}}{2.5}\right] + \left[\mathrm{C_{IC,i+2}}\left(\frac{\mathrm{V_E}}{\mathrm{m_{AFA}}}\right) - \frac{\mathrm{M_{AFA,i+1}}}{2.5}\right] \quad (3)$$

The results are presented in Table 6.

Table 6. Ammonia Content of AFA and FA Samples

Sample Identification	Average Ammonia Content ($mg-NH_3/kg-AFA$)	Standard Deviation
AFA-High	2760	80.1
AFA-Low	29.6	0.375
FA-High	1140	78.3
FA-Low	96	14.3

As shown in Table 6, the ammonia concentration in the AFA and FA samples covered a wide range of concentrations. AFA-High had the highest ammonia content of 2760 $mg-NH_3/kg-AFA$ with a standard deviation of 80.1 $mg-NH_3/kg-AFA$, while AFA-Low had the lowest concentration of 29.6 $mg-NH_3/kg-AFA$. Spiked FA samples were close to the theoretical concentrations with slight variations. AFA-High was subsequently used to assess ammonia extraction methods due to the following two reasons. 1) It is representative because it is an actual AFA sample. 2) Its high ammonia concentration will provide a conservative way to evaluate the capability of each extraction method. AFA-Low, FA-High, and FA-Low were used for method validations.

4.6. Batch Leaching Tests Using Syringe for Extraction

Batch leaching tests were used to determine the extent of ammonia leaching under varying sets of conditions. These conditions included: extraction solution, degree of agitation, extraction time, and L/S.

4.6.1. Influence of Extraction Solution and Agitation

Four different extraction solutions were investigated: DI water, 0.1 M acetic acid (AA), 0.1 M hydrochloric acid (HCl), and 2 M potassium chloride (KCl) solution. DI was selected because it has been shown to be effective on extracting ammonia from fly ash based on literature reviews (Ban, 2001; Wang et al., 2002). In addition, it is widely available and economical to use for the industry. AA and HCl were selected because they would reduce the extract pH and reduce ammonia volatilization during the extraction. If the extract pH is less than 7, ZHE would not be required for extraction. KCl was used because it is widely used as an extractant in soil analyses (Li et al., 2006). In addition to varying the extraction solutions, the degree of mixing was also evaluated: no-agitation, rotation, and shaking by using a shaker, as shown in Figure 6-8. All experiments were conducted in triplicate.

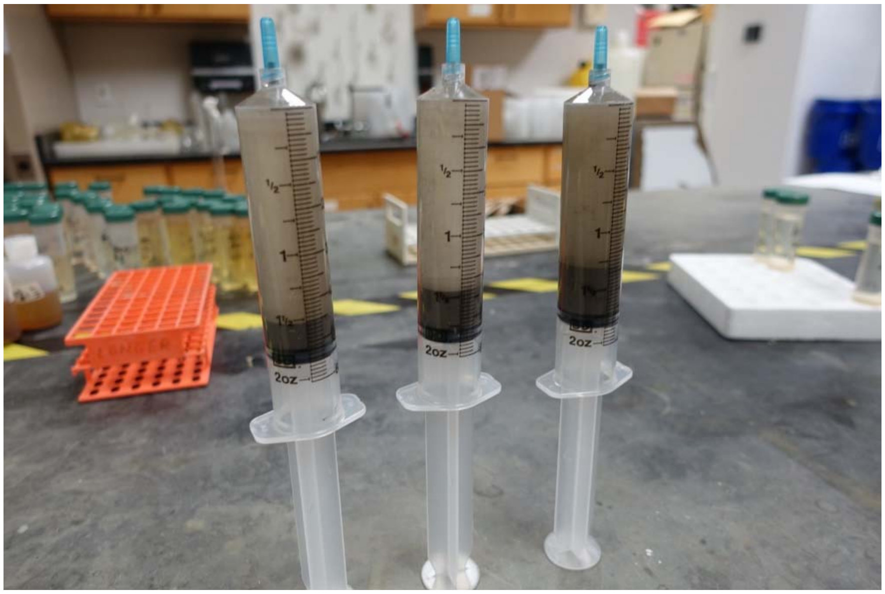

Figure 6. Extractions with no agitation

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Figure 7. Extractions by rotation

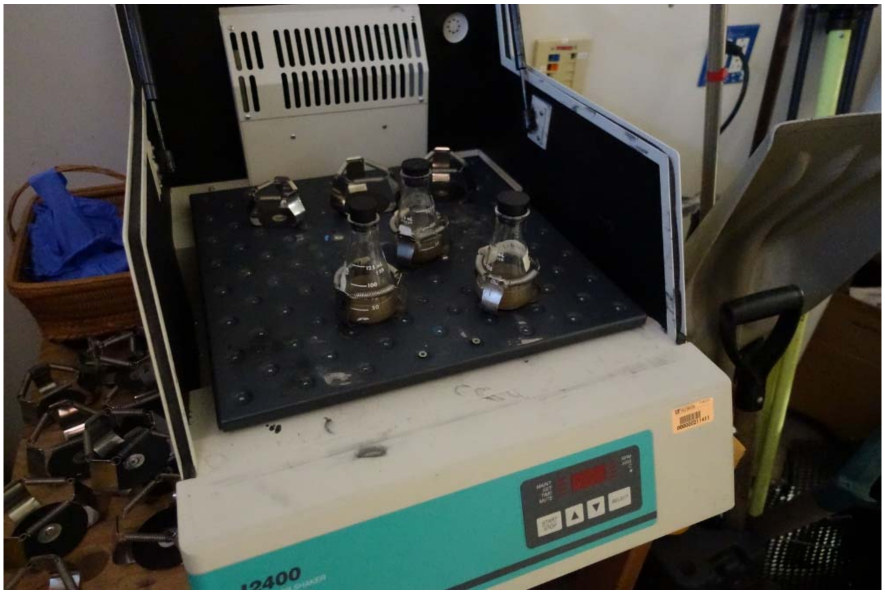


Figure 8. Extractions by shaking on a shaking table.

Parallel experiments were conducted to study the effect of different extraction solutions. For each experiment, 5 grams of AFA-High were placed in a syringe, and 50 mL of extraction solution (DI, AA, HCl, or KCl) was injected into the sample syringe using a syringe connector in an attempt to minimize headspace. All syringes were closed with syringe tip caps to prevent contact with air. Syringes were left stationary on the bench top for 1 hour before taking measurements of pH and ammonia concentration. For evaluating the effect of rotation, the same procedure was followed except that the syringes were mixed using a rotator at a constant speed for 1 hour. For evaluating the effect of shaking, 10 grams of sample and 100 mL of AA were placed in a 150-mL flask. AA was used to prevent ammonia escape into the headspace of the flask. Half of the flasks were left stationary on the bench top while the other half were placed on a shaker table for 1 hour. The pH and ammonia concentrations were measured immediately after the extraction. The results are presented in Table 7 and Figure 9 below, where subfix R refers to rotation, S refers to shaken, NS refers to non-shaken, and the rest of them were stationary.

Table 7. Summary of Ammonia Leaching Results (mg-NH_3/kg-AFA) with Different Extraction Solutions and Agitation Methods

Extraction Solution	**Agitation**	**Mean Concentration**	**Concentration Std.**	**Percent Extraction (%)**	**pH**	**pH Std.**
DI	N/A	706	48.3	25	10.8	0.049
DIR	R	2768	29.5	100	11.1	0.005
AA	N/A	1581	495.4	57	4.7	0.047
AAR	R	2758	80.8	100	4.6	0.005
AAS	S	1456	491.8	53	4.3	0.102
AANS	NS	1530	135.1	55	4.3	0.022
HCL	N/A	1595	595.8	58	1.6	0.113
HCLR	R	2482	145.6	90	2.3	0.017
KCL	N/A	1312	458.3	48	11.5	0.031

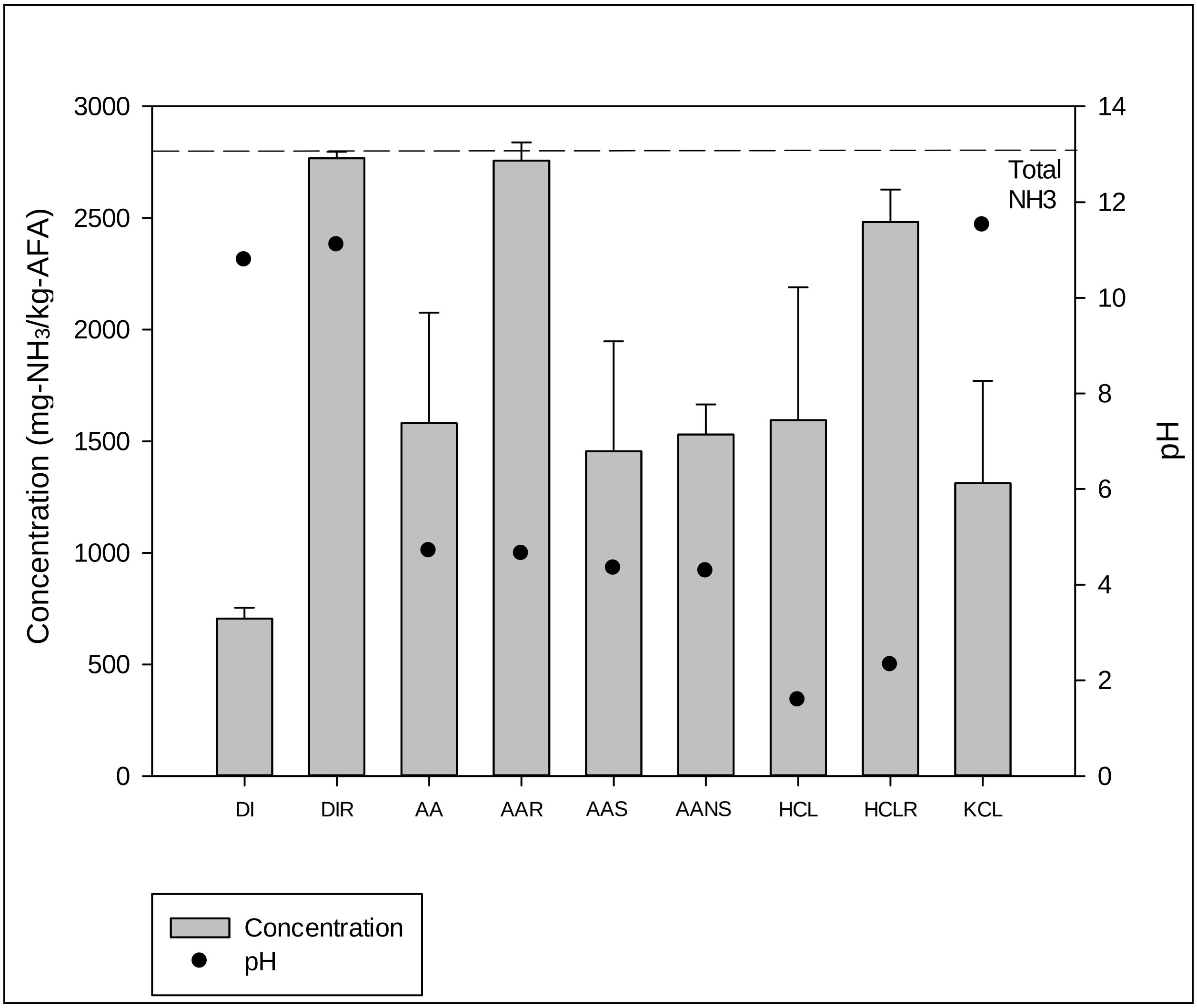


Figure 9. Ammonia concentrations (mg-NH_3/kg-AFA) in extracts from different extraction solutions (DI=DI water, AA= 0.1 M acetic acid, HCL=0.1 M hydrochloric acid, KCL=2 M potassium chloride) and agitation methods (subfix R refers to rotation, S refers to shaken, NS refers to non-shaken, and the rest of them were stationary).

When there was no agitation, results showed that AA and HCl were the most capable of extracting ammonia from fly ash, in comparison with DI and KCl. The pH of AA and HCl extracts were 4.7 and 1.6, respectively. Both solution pH values were below 7, which would prevent the formation of un-ionized ammonia. The pH of DI and KCl extracts were 10.8 and 11.5, respectively; high pH conditions increase the chance of ammonia gas escape during the measurement process, which potentially contributed to the DI and KCl's low extraction performances while there was no agitation. KCl extraction resulted in low extraction performance with high extract pH; therefore, it was eliminated as a suitable extraction solution candidate.

When the samples were rotated, the extraction performance of each extraction solution was significantly increased, with DI water showing an increase in the extraction of ammonia of 392% versus the stationary method. The significant improvements were likely caused by the increased liquid-solid contact (surface area) when the samples were well mixed. Figure 10 presents a picture of a non-agitated HCl sample. It can be seen that gas bubbles were entrapped in the fly ash samples at the bottom of the syringe, indicating low permeability and low liquid to solid contact area. As shown in Figure 9, DIR achieved similar extraction performance to AAR, while HClR fell slightly behind. The pH of DIR, AAR, and HClR extracts were 11.1, 4.6, and 2.3 respectively. When taking measurements on HCl extracts, it was noticed that ISE experienced rapid changes in reading before stabilization while measuring ammonia concentration in the extract, and it took longer for ISA to raise the extract pH to the condition that un-ionized ammonia can form. It was suspected that more metals leached into the extract with HClR due to its low pH, which could potentially cause interference with ISE probe. In addition, the ISE took longer to stabilize; it could result in more ammonia gas escape during the measurement process. Figure 11 illustrates that more precipitation were observed with HClR in comparison with AAR immediately after agitation.

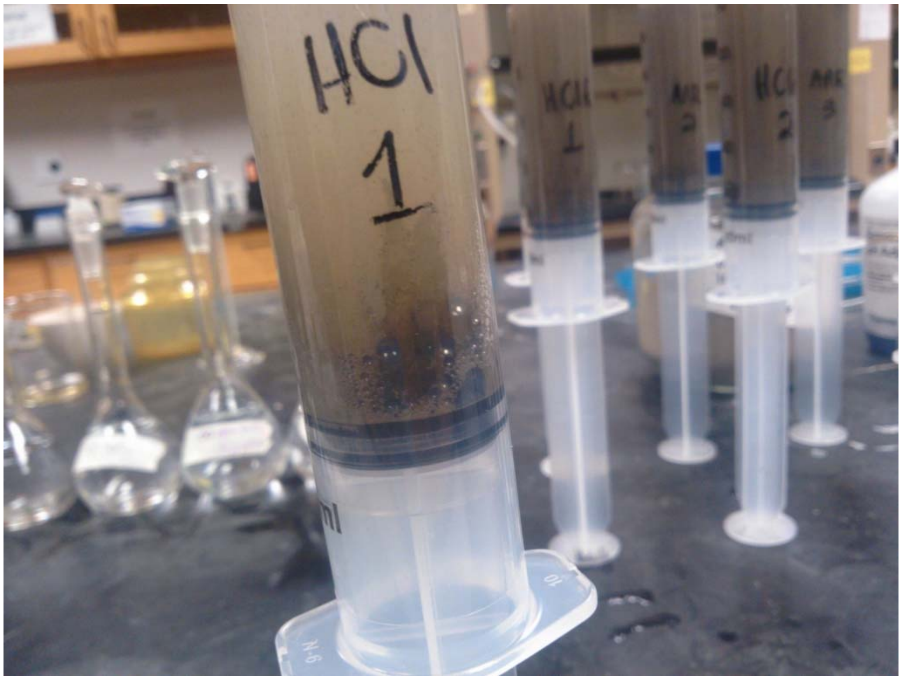
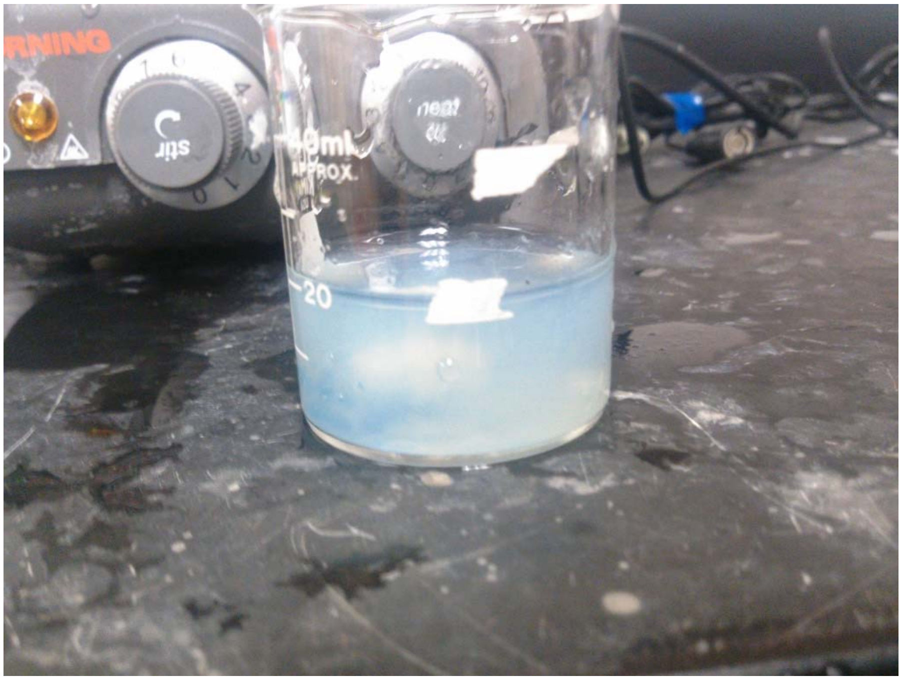


Figure 10. Air bubbles entrapped by fly ash in a non-agitated sample



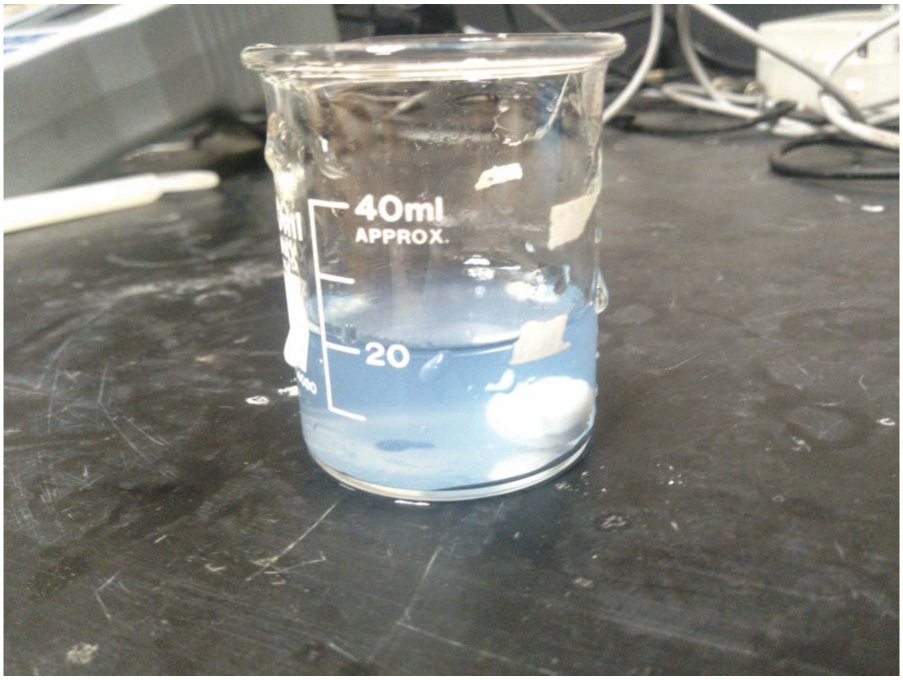


Figure 11. More precipitation formed in HCLR extract (top figure) than in AAR extract (bottom figure)

In conclusion, DI and AA performed the best among all the extraction solutions tested. Agitation is necessary to effectively extract ammonia from fly ash. DI and AA achieved similar extraction efficiency when the samples were agitated. KCl was eliminated as a potential candidate due to the high extract pH and low extraction efficiency. HCl was also eliminated because it did not perform as well as DI and AA. In addition, the use of HCl as extraction solution can potentially produce extract that would be hazardous waste (pH<2).

4.6.2. Influence of Liquid-to-Solid Ratio (L/S)

The effect of L/S on the extent of ammonia extraction from AFA was evaluated. It is known that ammonia present in the fly ash is highly soluble in the forms of ammonium sulfate and ammonium bisulfate (Ban, 2001; Wang et al., 2002). A few studies identified in the literature review used a L/S of 10:1 when extracting ammonia from fly ash, and achieved over 90%

extraction in 1 hour (Ban, 2001; Wang et al., 2002). However, it is important to study the effect of L/S on the extent of ammonia release and on other experimental and procedural parameters.

Experiments were conducted in similar procedures described in section 1.3.1 using syringes that were rotated. The conditions chosen for these experiments were 0.1 M Acetic Acid (AA) used at L/S of 5:1, 10:1, and 20:1. Due to the size of the syringe, the extract fluid was limited to 50 mL. Hence the mass of the solid was adjusted to 2.5 g, 5 g, and 10 g of AFA-High to achieve the targeted L/S. The extraction time was 18 hours. Table 8 and Figure 12 presents the results from L/S leaching tests:

Table 8. Summary of Ammonia Leaching Results (mg-NH_3/kg-AFA) with Different L/S Ratios

L/S	**Concentration**	**pH**	**pH Std.**
5:1-AA-18hr	2774 ± 33	6.75	0.08
10:1-AA-18hr	2752 ± 22	4.85	0.04
20:1-AA-18hr	2753 ± 76	4.31	0.00

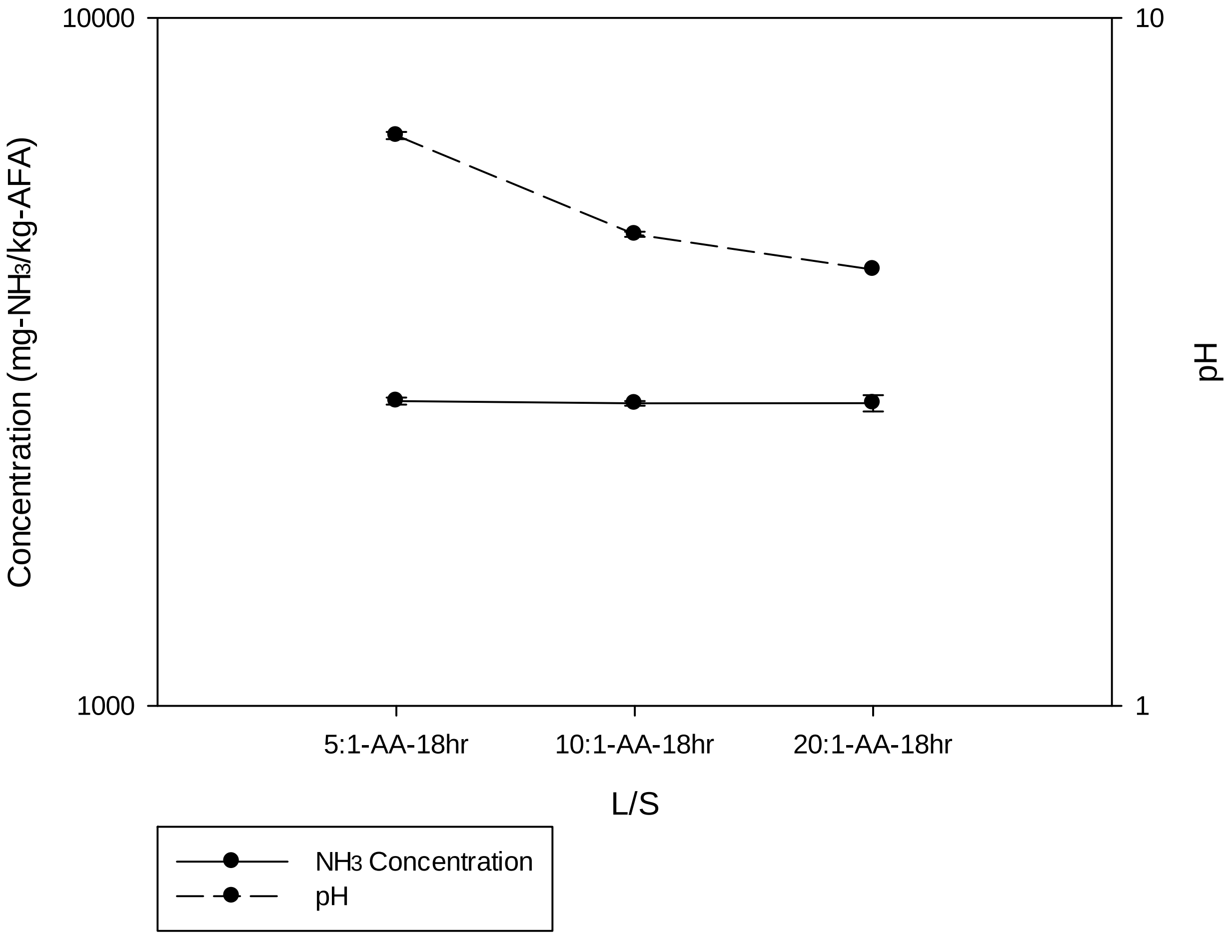


Figure 12. Ammonia leaching from AFA as a function of L/S

Results show similar concentrations were measured from samples extracted at different L/S, indicating ammonia in AFA is highly soluble. At room temperature, water can contain 31% ammonia. Ammonium sulfate has a solubility of 74.4 g/100 mL in water at room temperature. The ammonia concentration detected ranged from 14.1 to 56.1 g/100 mL, which remained much lower than the ammonium sulfate solubility limit. Because the ammonia and ammonium in the solution below the solubility limit, it does not produce any noticeable effect on the extent and the rate of ammonia leaching. Results also showed decreasing pH with increasing L/S. At L/S of 5:1, the pH (6.3) was found to be close to pH 7 when un-ionized ammonia can form. In addition, the standard deviations were found to be smaller at lower L/S when more AFA-High were used during the leaching test. Overall, an L/S of 10:1 was found to be optimal for extracting ammonia from AFA. It can effectively extract ammonia from AFA with AA while producing a slightly acidic extract that would prevent the gaseous ammonia from releasing into the ambient air.

4.6.3. Influence of Extraction Time

Results from previous studies indicated that ammonia release from fly ash is rapid. Five different time intervals were selected to evaluate ammonia leaching as a function of time: 10 min, 30 min, 1 hr, 5 hrs, and 18 hrs. The results were used to determine the optimal time for ammonia extraction from AFA. Extraction procedures were consistent with those described in section 1.3.1, except that variable extraction intervals were used. The extraction solutions used were DI and AA. Results are summarized in Table 9 presented below.

Table 9. Summary of Ammonia Leaching Results with Different Extraction Time

	DI			**AA**		
Time	Concentration (mg-NH_3/kg-AFA)	% Extraction	pH	Concentration (mg-NH_3/kg-AFA)	% Extraction	pH
10 min	2052 ± 160	74	11.0	2176 ± 88	79	4.66
30 min	2623 ± 92	95	11.3	2660 ± 223	96	4.71
1 hour	2768 ± 29	100	11.1	2758 ± 81	100	4.64
5 hours	2709 ± 11	98	11.4	2631 ± 67	95	4.83
18 hours	2747 ± 27	100	11.5	2846 ± 39	103	4.85

It can be seen from the table that about 80% of the ammonia content was released within 10 minute of extraction, and 100% of the ammonia content was released in 1 hour. After 1 hour the solution reached equilibrium with a concentration of approximately 270 mg-NH_4^+/L, which is equivalent to 2700 mg-NH_3/kg-AFA. The extract pH increased with time, however only slightly. The results aligned with those found in the literature review. Ammonia can rapidly leach from AFA. In the industrial or laboratory scenarios, the fast dissolution of ammonia and ammonium salts would favors the engineers and the scientists in testing ammonia content in fly ash, allowing them to conduct rapid extract and process large amount of samples.

4.7. Batch Leaching Tests Using Open Container for Extraction

In Section 1.3 it was determined that DI and AA are potential candidates for extraction solutions; agitation is necessary for fast and effective extraction; L/S=10:1 is optimal for extraction; and ammonia leach almost immediately in a matter of minutes. One of the goals for this project is to develop an effective method that can also minimize the cost of the analysis. Ammonia in AFA was found to release quickly in the AA extraction solution, and the extract pH is less than 7. Therefore it is possible to use an open container such as a breaker for extraction. Therefore the use of syringe, syringe filter, and syringe tips can be eliminated. As a result, the running cost of analysis will be minimized. Batch leaching tests were conducted using an open container. AA extraction solution and a L/S=10 were used because they were found to be effective. As shown in Figure 13, a 60 mL breaker was used to hold 5 grams of AFA-High, AFA-Low, FA-High, or FA-Low sample. Then 50 mL of DI or AA solution was added into the beaker. The beaker was placed on a stir plate with a magmatic stirrer stirring the sample at a moderate speed. The experiment was conducted in two different ways: 1) 1 mL of ISA was added immediately after placing the breaker on the stir plate. An ammonia ISE was used to continuously measure the level of ammonia until the concentration start to decrease. 2) Samples were allowed to be stirred for 5 mins before adding ISA and taking measurement with an ISE. Results from the experiments are summarized below in Table 10 and Figure 14 below.

Figure 13. Extraction using a 60-mL beaker

Table 10. Summary of Results (mg-NH_3/kg-AFA) from Batching Leaching Tests Using an Open Container

Sample	**Continuous**	**% Release**	**5 Minute**	**% Release**
AFA-High (DI)	2590 ± 34	94	2254 ± 25	82
AFA-High (AA)	2621 ± 23	95	2610 ± 31	95
AFA-Low(DI)	25.0 ± 0.31	85	25.3 ± 1.08	84
AFA-Low(AA)	26.3 ± 1.96	92	27.1 ± 1.16	89
FA-High(DI)	1094 ± 24	96	945 ± 73	83
FA-High(AA)	1071 ± 15	94	1118 ± 26	98
FA-Low(DI)	93.1 ± 0.35	97	83.0 ± 3.42	86
FA-Low(AA)	91.5 ± 1.04	95	92.1 ± 2.44	96

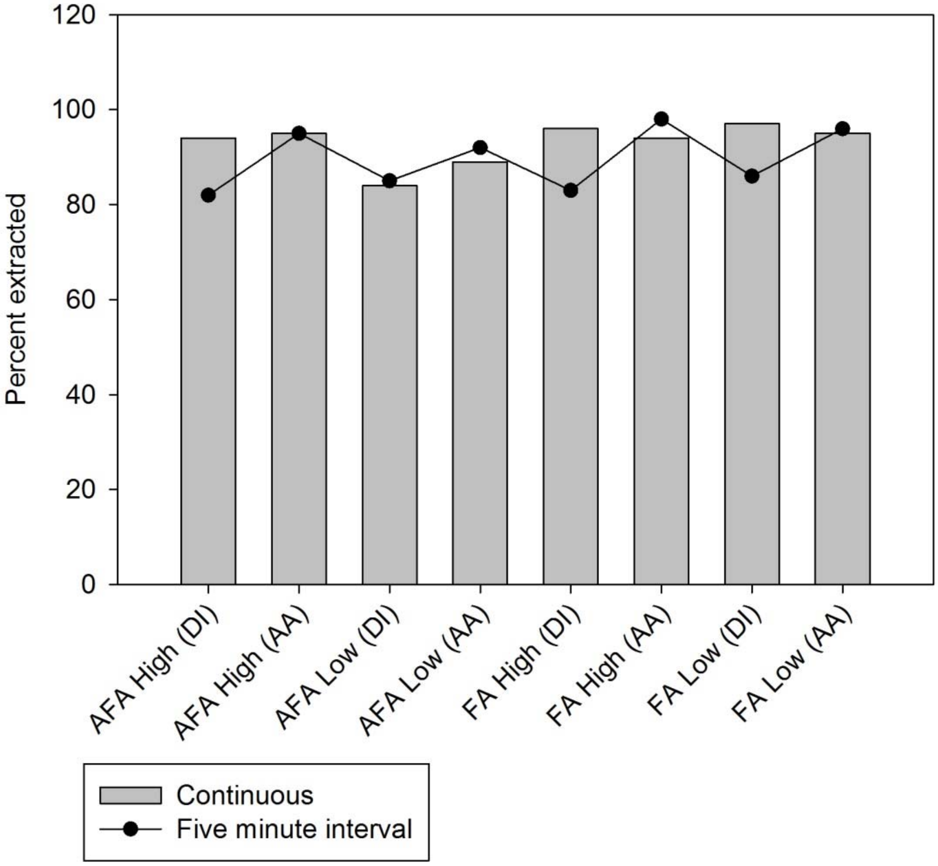


Figure 14. Measured percent extraction for all samples using continuous method and 5-minute method.

Results showed that extraction using open containers is very effective in extracting ammonia from AFA; all samples achieved at least 80% extraction efficiency, mostly at a level above 90%. When the sample was extracted while being continuously measured with ISE, it was found that ISE stabilized within 2 minute. Both DI water and AA achieved similar extraction efficiency at over 95%. However, DI water had noticeably lower extraction efficiency in comparison with AA while using the 5 minute extraction method. It is mostly caused by ammonia release to the ambient air because the extracts' pH were over 10 for most DI extracts, while the pH of AA extracts were below 5. AA in the 5 minute extraction method had similar extraction efficiency when compared to the continuous method at a level of approximately 95%. From a conservative perspective, the 5 minute extraction method with AA extraction solution appears to be the best method for the open container testing. Results demonstrated that AA can achieve high extraction efficiency in a short period of time while ensuring the extract has a slightly acidic pH minimizing loss of gaseous NH_3. It would also allow the analyst to store and preserve samples if immediate analysis is not available.

4.8. Extraction Using a 50 mL Centrifuge Tube

Experiments were conducted to further reduce the cost of extraction. In this experiment, 5 grams of material and 50 mL of AA were added to a 50 mL centrifuge tube, as shown in Figure 15. There was approximately 5 mL of headspace left allowing for agitation by shaking. The tube was then shaken by hand for 30 seconds before tested by the ISE. The results are presented in the Table 11 below.

Figure 15. Extraction using a 50-mL centrifuge tube.

Table 11. Summary of Results from Extraction tests Conducted Using Centrifuge Tubes

Sample	**Concentration (mg/kg)**	**% Release**
AFA-High (AA)	2378 ± 33	88
AFA-Low(AA)	29 ± 0.19	98

Results show that this extraction method effectively extracted 88% of the ammonia content from AFA-High, and 98% content from AFA-Low. The centrifuge tube extraction method reduces the cost of stir plate, stir bar, and beaker. It's a simpler experimental setup in comparison with the open container extraction method.

4.9. Conclusions

During Task 3, experiments were conducted to determine the optimal extraction conditions for the transfer of ammonia from the solid phase (the AFA) into the liquid phase (the extract, which will be needed for most analytical techniques). Laboratory tests were conducted to evaluate the influence of a variety of extraction parameters on extraction efficiency. These factors included: liquid-to-solid ratio (L/S), extraction solution, extraction time, degree of agitation, sample processing, chemicals used, and cost.

The results suggested that both DI and 0.1 M AA solution have high extraction effectiveness. The use of AA resulted in high extraction efficiency while maintaining the extract pH below 7, at which point, un-ionized ammonia cannot form. It would allow analysts to use non-zero-headspace devices such as a beaker or a centrifuge tube for extraction, therefore eliminating the cost to purchase ZHE (or syringe) and syringe filter, if analyzed with ISE. The extracts can be stored for later analysis if immediately analysis is not available. Although DI water achieved similar extraction efficiency in many tests, ammonia loss during experiment is possible because the extract pH is higher than 7. The use of ZHE or syringes would be the preferred method for extraction if DI water is used. The use of ZHE or syringes will result in higher cost for the extraction.

Leaching results at different L/S suggested that the ammonium salts present in the AFA were highly soluble. There was no noticeable difference for ammonia concentrations measured at L/S = 5:1, 10:1, and 20:1. However, the pH at L/S = 5:1 was the highest at a level close to pH=7 (AA as extraction solution). If the AFA sample has high natural pH, there is a chance for the extract to exceed pH=7.

For degree of agitation, results suggested that rotation will significantly improve the extraction efficiency while using a syringe. When the extraction is conducted with AA in a beaker or a centrifuge tube, agitation with a stirrer on the stir plate or simply shaking by hand was proven to be highly effective.

5. Non-Extraction Methods

Potential methods which do not use extraction will be considered. This may include liberating gaseous ammonia from the solid AFA or other nontraditional or micro techniques.

5.1. Potential Non-Extraction Methods

Known procedures to determine the amount of ammonia contained in coal fly ash without extracting the ash with a solvent (and assaying the extract), rely on liberating the ammonia and quantifying the released gas.

5.2. Measuring Ammonia Concentration in AFA by Gas Sampling Tubes (Used by Headwaters Resources)

A derivative of this method is used by Headwaters Resources who handles the assay for ash management within the Southern Company. Headwaters is one of the nation’s leading ash suppliers.

A sample of fly ash and a measured amount of water is added to a clean 1 L Erlenmeyer flask with a stir bar. After mixing for one minute, an aliquot of aqueous sodium hydroxide is added to bring the pH above 12. The flask is immediately stoppered with a two-hole stopper which was previously fitted with an ammonia detector tube and a manual gas sampling pump (specific for the brand of tube used). After a short stirring period, the headspace gas is measured by actuation of the pump and reading ammonia concentration result on the tube. A multiplier is applied to the result based on a standard curve.

Advantages of the non-extraction methods for the purposes of this study included the fact that a direct measurement of the liberated gas is made. The physical thermodynamics of partitioning the ammonia from the condensed phases of solid and/or liquid to the gas phase is related to the real world situation in which the project objectives were based- that is to say, when ammoniated fly ash is an additive to portland cement, the addition of water to form concrete causes the same release of gaseous ammonia. An additional advantage of the non-extraction methods is the avoidance of solute interferences often experienced with solution measurements.

5.3. Summary

Gas phase measurement of released ammonia is a good candidate for a Standard Operating Procedure.

6. Ammonia Analysis Technique Assessment

This section of the report describes the evaluation of a variety of different analytical testing techniques, including ammonia ion-selective electrode, ion chromatography, and colorimetric methods. The ability of the different analytical techniques to accurately and precisely measure ammonia in the extracts were compared, with due consideration of analytical cost, analysis time, reparability, and training or expertise needed.

6.1. Ammonia Ion-Selective Electrode (ISE)

6.1.1. Summary of Test Method

The ISE method is included in the ASTM D1426 for the measurement of ammonia nitrogen in water. It is also referenced in the ASTM C 311 for the measurement of ammonia content in coal fly ash. The ammonia ISE uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. Ammonia diffusing through the membrane dissolves into the ISE filling solution.

The filling solution contains ammonium chloride, and the electrode will measure the electric potential of the filling solution. The electrode potential measured by the ISE is proportional to the ammonia concentration in the sample. The range of detection for the ISE method is 0.01 to 17,000 mg/L as NH_3. Volatile amines can interfere with electrode measurements. Some metallic ions complex ammonia, causing falsely low results in direct measurements. The pH-adjusting ISA removes interferences from metallic ions. If the pH meter is used, the ammonia concentration is determined from a calibration curve; if the ISE meter is used, the ammonia concentration is directly read from the meter.

6.1.2. Apparatus

Apparatus used in the extraction and analysis of ammonia using the ISE method include:

- 60 mL Beaker
- 60 mL Syringe
- 0.45 µm Nylon Syringe Filter
- 100 mL Graduated Cylinder
- Parafilm
- Magnetic Stirrer
- Stir Bar
- Pipet 0.1 to 1.0 mL
- Pipet Tips 0.1 to 1.0 mL

6.1.3. Chemicals Used

Chemicals used in the extraction and analysis, and O&M of the ISE method include:

- 0.1 M Acetic Acid
- Ammonia Standard Solution (1000 mg NH_3 as N/L)
- pH-Adjusting Ionic Strength Adjuster (ISA)
- Electrode Filling Solution
- Alkaline Reagent (low-level ISA)

- Deionized Water

6.1.4. Ammonia Extraction from Fly Ash

Ammonia was extracted from three fly ash samples: AFA High (approx. 2500 mg-NH_3/kg-AFA), AFA Low (approx. 35 mg-NH_3/kg-AFA), and FA-120 (approx. 35 mg-NH_3/kg-FA). Batch leaching extraction was conducted using a 60 mL beaker. The extraction procedure was selected from the previous task based on its optimal extraction performance (refer to Task 3 Report). The extraction method was slightly modified to improve its extraction efficiency.

A five-gram sample of fly ash was weighed using a digital scale. Acetic acid stock solution was used to prepare 0.1 M acetic acid solution (0.1 M AA) for the extraction. A 60 mL borosilicate glass beaker was placed on a stirrer and 50 mL of 0.1 M AA solution was added into the beaker. A magnetic stir bar was then placed in the beaker to stir the solution at a moderate rate. The 5 gram fly ash sample was slowly added into the beaker and Parafilm was immediately used to seal the beaker to prevent possible ammonia escape. The fly ash slurry was mixed as described for 5 min before a measurement was taken.

6.1.5. Ammonia Analysis Using the ISE Method

A four-point calibration that brackets the expected concentration was conducted prior to the extraction procedure. After the extraction, 20 mL of the extract was filtered using a 60 mL syringe and a 0.45 µm nylon syringe filter into another 60 mL beaker. The pH adjusting ISA (0.4 mL) was then added and the measurement was taken immediately while it was being stirred at a moderate rate. The pH of the solution was also measured at this point. The ammonia concentration was then determined from the calibration curve.

6.1.5.1 Analysis Cost

The capital and operational costs were analyzed. The results were normalized to cost per sample for comparison with other analysis methods.

An estimation of the capital cost for analysis using the ISE method is shown in Table 12.

Table 12. Capital Cost for Analysis Using Ammonia ISE

Item	**Cost ($)**
60 mL Beaker	5
60 mL Syringe	0.75
0.45 µm Nylon Syringe Filter	1.4
100 mL Graduated Cylinder	35
Parafilm	100
Magnetic Stirrer	195
Stir Bar	10
Orion Ammonia ISE	600
pH/mV Meter	700
Four 100 mL Volumetric Flask	340
Acetic Acid Stock Solution	77
Ammonia Standard Solution (1000 ppm)	65
pH-Adjusting Ionic Strength Adjuster	121
Electrode Filling Solution	80
Alkaline Reagent (Low-Level ISA)	40
Pipet	250
Pipet Tips (1000 tips)	100
Total	**2,370**

In comparison with other methods tested, the capital cost of ISE method is relatively high ($2,430). The operational cost for the analysis is estimated at $0.70 per sample, which is the lowest among all methods tested.

6.1.5.2 Analysis Time

An estimation of the time required for the analysis using the ISE method is presented in Table 13. The procedures were divided into two categories – preparation and measurement.

Table 13. Analysis Time for Each of the Procedure Using the ISE Method

Procedure	**Time (min)**
Preparation - Ammonia Standard Preparation	10
Preparation - Calibration	5
Measurement - Weighing Samples	1
Measurement - Extraction	7
Measurement - Analysis	1

The preparation of the experiment takes approximately 15 min. Once it is prepared, measurement takes approximately 9 min per sample. The ISE method takes a relatively long time for standard preparation and calibration. In addition, it is recommended to check or recalibrate the probe every one hour.

6.1.5.3 Repeatability

The experiments were conducted in six replicates. The percent error for each sample are presented in Table 14.

Table 14. Percent Error from Analysis Using the ISE Method

	AFA-High	**AFA-Low**	**FA-120**
ISE Percent Error	7.73%	7.67%	5.21%

The percent errors were within 8% for all samples tested and suggested that the repeatability of the ISE method was high.

6.1.5.4 Training and Expertise Requirement

The technical skills required for using the ISE method are relatively high in comparison with other methods tested. The technician will need to be trained in preparing calibration standards, calibrating of the instrument, proper and safe handling of chemicals, and operation and maintenance of the ISE probe and pH meter.

6.2. Ion Chromatography (IC)

IC is used for a wide range of applications, including the determination of ionic solutes such as inorganic anions, cations, metals, and low-molecular-weight organic acids and bases. It can also be used for a wide range of matrices such as drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, and solids extract. The range of detection for ammonia is 0.05 – 40 mg/L.

The basic process of IC can be presented in the following steps: eluent loading, sample injection, separation of sample, and elution of analytes. During the process, separation of ions and polar molecules occur based on their affinity for the ion exchanger. A small volume of sample (2-3 mL) is introduced into an IC. The anion of interest are separated and measured, using a system comprised of guard column, analytical column, and suppressor device and conductivity detector.

A typical chromatography system consist of the following parts:

- Gradient pump
- Eluent generator
- Cartridge
- Electrochemical detector with conductivity cell and detector stabilizer
- Automated Sampler
- Chromatography Software
- Syringe
- Syringe Filters

The goal of the project is to identify a methodology that provides an accurate measurement of ammonia concentration in coal fly ash and can be readily and economically performed by end users with broad ranges of skills. With the consideration of the high capital cost (approx. $50,000) and the extensive training and knowledge required to properly operate and maintain the IC system, the IC method will not be further discussed.

6.3. HACH DR/4000 Spectrometer Procedure - Ammonia Nitrogen

6.3.1. Summary of the Method

This method is applicable for the determination of NH_3-N in water, wastewater, and seawater. Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound. The blue color is masked by the yellow color from the excess reagent present to give a green-colored solution. The spectrometer measures the intensity of the light beam going through the solution as a function of its color (wavelength). The detection range for this method is 0 – 50.0 mg/L NH_3-N. Interferences can be caused by pH, calcium (50,000 mg/L as $CaCO_3$), glycine, hydrazine, magnesium (300,000 mg/L as $CaCO_3$), iron, nitrite (600 mg/L as NO_2^- - N), nitrate (5,000 mg/L as NO_3^- - N), orthophosphate (5,000 mg/L as PO_4^{3-} - P, sulfate (6,000 mg/L as SO_4^{2-}), sulfide and turbidity and color.

6.3.2. Apparatus

The apparatus used in the extraction and analysis of ammonia using the HACH Spectrometer method include:

- High Range Test ‘N Tube AmVer Nitrogen Ammonia Reagent Set
  - AmVer Reagent HR TNT Vials
  - Ammonia Salicylate Reagent Powder Pillows
  - Ammonia Cyanurate Reagent Powder Pillows
- HACH DR 4000 Spectrometer
- DR 4000 Test Tube Adapter
- Pipet 0.1 to 1.0 mL
- Pipet Tips 0.1 to 1.0 mL
- 60 mL Syringe
- 0.45 µm Nylon Syringe
- pH Meter

6.3.3. Chemicals Used

Chemicals used in the extraction, analysis, and the O&M of the HACH Spectrometer include:

- Hydrochloric Acid ACS
- Ammonia Standard Solution 1000 ppm
- Deionized Water (DI)

6.3.4. Ammonia Extraction from Fly Ash

Ammonia was extracted from two fly ash samples: AFA High (approx. 2500 mg-NH_3/kg-AFA) and AFA Low. The extraction was conducted based on the Centrifuge Tube method. Five grams of material and 50 mL of DI water were added to a 50 mL centrifuge tube. There was approximately 5 mL of headspace left allowing for agitation by shaking. The tube was then vigorously shaken by hand for 30 seconds.

6.3.5. Ammonia Analysis Using the Spectrometer Method

After the extraction, the samples were first filtered using the 60 mL syringe and 0.45 µm nylon syringe filter. The pH was immediately taken after filtration. Hydrochloric acid was used to titrate the pH to approximately 7. Since the range of detection is 0 – 50.0 mg/L NH_3-N, the AFA High sample extract was diluted 10 times. The analysis program (2465 N, Ammonia HR TNT) was first loaded on the HACH Spectrometer. The caps were removed from two AmVer reagent vials. Then 0.1 mL of DI into one vial (blank), and 0.1 mL of sample was added into another vial (the sample). One powder pillow of ammonia salicylate reagent, followed by one powder pillow of ammonia cyanurate reagent, was added to each vial. The caps were placed back on to the vials and the vials were shaken thoroughly to dissolve the powder. After 20 minute reaction period, the blank sample was first placed into the DR 4000 Spectrometer to zero the machine. Then, the sample was placed into the machine and the result in mg/L ammonia nitrogen was displayed on the screen.

6.3.5.1 Analysis Cost

The capital cost and the operational cost were analyzed. The results were normalized to cost per sample for comparison with other analysis methods.

An estimation of the capital cost for analysis using the spectrometer method is shown in Table 15.

Table 15. Capital Cost for Analysis Using the HACH DR 4000 Spectrometer

Item	**Cost ($)**
High Range Test 'N Tube AmVer Nitrogen Ammonia Reagent Set	93
HACH DR 4000 Spectrometer	4000
0.45 µm Nylon Syringe Filter	1.4
60 mL Syringe	0.75
Test Tube Adapter	90
Pipet 0.1-1 mL	250
Pipet Tips 0.1-1 mL (1000 tips)	100
Ammonia Standard Solution (1000 ppm)	65
Hydrochloric Acid ACS 2.5 L	125
pH meter	5225
Total	**4725**

In comparison with other methods tested, the capital cost of ISE method is high at $5,225. The operational cost for this analysis is estimated at $4 per sample, which is the highest operational cost among the analysis methods involving ammonia extraction.

6.3.5.2 Analysis Time

An estimation of the time required for the analysis using the spectrometer method is presented in Table 16.

Table 16. Analysis Time for Each of the Procedures Using the Spectrophotometer Method

Procedure	**Time (min)**
Measurement - Weighing Samples	1
Measurement – Extraction	0.5
Measurement – Analysis	25

The whole measurement process of analysis of one sample takes approximately 27 minutes. However, the user can prepare multiple samples at the same time to save time. No calibration is needed in the spectrometer method therefore the time required to prepare standards and calibrate is eliminated.

6.3.5.3 Repeatability

The experiments were conducted in triplicate. The percent error are presented in Table 17.

Table 17. Percent Error from Analysis Using the Spectrophotometer Method

	AFA-High	AFA-Low
ISE Percent Error	5.00%	2.37%

The percent errors were within 5% for all samples tested and suggests that the repeatability of the spectrometer method is high.

6.3.5.4 Training and Expertise Requirement

The technical skills required for using the spectrometer method is relatively high in comparison with other methods tested. The technician will need to be trained for ammonia extraction, pH meter calibration, titration, and the operation of the spectrometer. Lab safety precautions also need to be taken into account when titrating with hydrochloric acid.

6.4. Salicylate Color Disc Kit Method

This method is applicable to measure ammonia concentrations in reagent and effluent water.

6.4.1. Summary of Test Method

Ammoniated fly ash extract containing aqueous ammonia is transferred into a clear glass tube and a powder pillow of sodium salicylate is added to the solution. After the salicylate salt is dissolved in solution, a powder pillow of ammonium cyanurate is added to produce the color change reaction. After 15 min, the vial is placed in the color comparator box beside another vial containing no color change reagents. The color wheel within the comparator box is then rotated until the color of the reagent containing sample best matches that of the color wheel section. The matched color section on the wheel corresponds to an aqueous concentration of ammonia in the solution.

This method is most applicable to samples with lower range ammonia nitrogen concentrations. After the addition of the ammonia salicylate powder pillow to the extract, ammonia in solution combines with hypochlorite to form monochloramine that reacts with salicylate to form 5-aminosalicylate. After the addition of the ammonia cyanurate powder pillow, 5-aminosalicylate is oxidized in the presence of a catalyst, nitroprusside or $Fe(CN)_5NO_2$- (also called nitroferricyanide) to form indosalicylate, a blue-colored compound. The blue color combined with the yellow color from excess nitroprusside forms a green-colored solution. The intensity of the color is directly proportional to the ammonia concentration.

6.4.2. Apparatus

The materials used in the extraction and analysis of ammonia using the color disc method include:

- 50 mL Centrifuge Tube
- 5 mL Syringe
- 0.45 µm Nylon Syringe Filter

- Hach Ammonia Nitrogen Color Disc Test Kit 0 to 2.5 mg/L as NH_3-N
    - Color Comparator Box
    - Reagents, ammonia cyanurate and ammonia salicylate powder pillows
    - Color Viewing Tube, glass
    - Stoppers, for class viewing tubes

6.4.3. Ammonia Extraction from Fly Ash

Ammonia was extracted from three fly ash samples: AFA High (approx. 2500 mg-NH_3/kg-AFA), AFA Low (approx. 35 mg-NH_3/kg-AFA), and FA-120 (approx. 35 mg-NH_3/kg-FA). One gram of ash was placed in a 50 ml centrifuge tube and filled with DI water to a final volume of 50 ml. The centrifuge tube was capped and shaken vigorously by hand for 30 seconds. The centrifuge tube was then uncapped and the ash slurry was drawn up into a 10 ml syringe. A syringe filter was attached to the syringe and the slurry was forced through the filter. Syringe filtrate was used for analysis.

6.4.4. Ammonia Analysis Using the Color Disc Method

For coal fly ash sample with less than 125 mg/kg ammonia, two color viewing tubes received 5 ml of filtered extract. One of the tubes was inserted into the left opening of the comparator. One powder pillow of ammonia salicylate was added to the other tube. The tube was capped, shaken to dissolve the reagent, and allowed to stand for 3 minutes. A powder pillow of ammonia cyanurate was then added to the same tube that was capped and shaken to dissolve the reagent. After 15 minutes, the tube was inserted into the right opening of the comparator. The comparator was held in front of a uniform light source so that that light was directly behind the tubes. The color disc was rotated until the two color windows matched and a concentration in mg/L was read. For coal fly ash sample with more than 125 mg/kg ammonia, 2.5 ml of DI water and 2.5 ml of the extract was transferred to each of the tubes and the same procedure was performed. The reading from the color disc was multiplied by two to determine the actual concentration in the extract.

6.4.4.1 Analysis Cost

The capital cost and the operational cost were analyzed. The results were normalized to cost per sample for comparison with other analysis methods. In comparison with other methods tested, the capital cost of the color disc method is lowest.

Estimated analysis costs for the Color Disc method are shown in Table 18.

Table 18. Cost Analysis for Color Disc Method

Hach Ammonia Nitrogen Color Disc Test Kit (0 to 2.5 mg/L as NH_3-N)	$90
Syringe and Syringe filter	$3.4 per sample

6.4.4.2 Analysis Time

An estimate of the time required for the analysis using the color disc method is presented in Table 19. The procedures were divided into two categories – preparation and measurement. No preparation steps are necessary for the color disc method.

Table 19. Procedure Durations for Analysis using the Color Disc Method.

Procedure	**Time (min)**
Measurement - Weighing Sample	1
Measurement – Extraction	4
Measurement – Analysis	20

6.4.4.3 Repeatability

The experiments were conducted in six replicates. The percent error for each ash type is presented in Table 20.

Table 20. Percent Error for Samples Analyzed using the Color Disc Method

	AFA-High	**AFA-Low**	**FA-120**
Color Disc Percent Error	5.21%	5.70%	5.66%

The percent errors were within 6% for all samples tested and suggests that the repeatability of the color disc method is high.

6.4.4.4 Training and Expertise Requirement

The HACH color disc kit has simple components and is easy to operate. Adjusting for interferences may be unlikely when testing coal fly ash extracts but may require some technical experience and additional resources.

7. Refined Test Method Comparison

Additional comparative testing was conducted with three selected methods (ISE, color disc, and gas tube). Spiked samples of fly ash that contained a known concentration of ammonia were prepared for this phase of testing. This allowed for an assessment of accuracy by determining the percent recovery of ammonia for each method. Nessler color disc method results obtained from the subsequent beta testing visit (discussed in Section 10) are also included to provide a more complete comparison. This section also presents comparative precision, cost, and test duration data.

7.1. Accuracy

The accuracy of each method was assessed by testing two fly ash samples (known to originally contain no ammonia) that were spiked with powdered ammonium sulfate. The measured and expected concentrations of ammonia were compared and a percent recovery was calculated for each method. A gas tube method measurement of a 75 mg NH_3/kg-AFA spiked fly ash sample was necessary as a 50 mg NH_3/kg-AFA ash was used for the development of the calibration curve. Results are presented in Table 21.

Table 21. Percent Recovery for the Testing Methods Assessed.

Spiked Ash (mg NH_3/kg-AFA)	**50**	**75**	**100**
ISE	83.6%	-	119%
Salicylate Color Disc	53%	-	70%
Salicylate (Spectrometer)	99%	-	67%
Gas Detection Tube	-	95%	104%
Nessler Color Disc Method (Beta Testing)			99%

It was observed that the color disk method had the least favorable percent recovery. Testing the same samples with a spectrophotometer showed that difficulty matching the sample color to the color wheel was likely the source of the error, particularly for the ash with lower ammonia concentrations (50 mg NH_3/kg-AFA). The ion selective electrode method showed recoveries within 20%. The gas tube method yielded the most favorable percent recovery compared to the other methods. Nessler Color disc results were obtained during the beta testing visit. This method was not initially selected for comparative testing due to the use of mercury containing Nessler's reagent and an effort was made to identify alternative methods.

7.2. Precision

The gas tube method produced the most consistent results between replicates. The color disk method had the highest variability between replicates. Percent relative standard deviation values for each method are shown in Table 22.

Table 22. Percent Relative Standard Deviation for each Method

Spiked Ash **(mg NH_3/kg-AFA)**	**50**	**75**	**100**	**Ash Product**
ISE	8%	-	8%	-
Salicylate Color Disc	11%	-	14%	-
Salicylate (Spectrometer)	9%	-	6%	-
Gas Detection Tube	-	4%	4%	5%
Nessler Color Disc (Beta Testing)	-	-	2%	14%

It was also observed that when conducting tests with colorimetric methods, readings varied between analysts. Independent readings from three analysts using the salicylate color disc method for different fly ash samples were recorded to assess the range of variability. These results are found in Table 23.

Table 23. Salicylate Color Disc Method Readings from Different Analysts for three Fly Ash Samples. Units of color disc method measurements are in mg/L NH_3 -N.

	Analyst 1	**Analyst 2**	**Analyst 3**
Sample A	0.4	0.6	0.5
Sample A	0.3	0.4	0.3
Sample A	0.4	0.4	0.4
Sample B	0.8	0.8	0.9
Sample B	0.8	0.8	0.8
Sample C	1.8	1.6	1.4
Sample C	1.6	1.6	1.8

The salicylate color disc has a color shade for each 0.2 ppm interval and a total range from 0 to 2 ppm. Readings would sometimes differ by 0.2 ppm on the color wheel between analysts at concentrations below 1 ppm aqueous ammonia and up to 0.4 ppm for concentrations above 1 ppm aqueous ammonia. This variability translates to 10 and 20 ppm differences in measured ash concentrations between analysts, respectively. The maximum observed variation between Nessler color disc readings was 0.2 ppm between three different analysts. This translates to approximately an 8 mg/kg variation in ash ammonia concentration. No variability for gas tube readings was observed between analysts. This was attributed to the well defined color change "front" produced within the tube that is measured against the tube graduations.

7.3. Cost Analysis

Estimated capital and running costs for each method are compared in Table 24. The ion selective electrode method had both the highest capital cost as well as the lowest running costs. The gas tube method had the second highest capital cost, and had slightly higher, but similar running costs to the salicylate and Nessler color disc methods. The difference in running costs between the gas tube and the color disc methods is not considered to be prohibitive to the use of the gas tube method.

Table 24. Capital and Running Cost for each Method.

Methods	**Capital Cost**	**Running Cost (per sample)**
ISE	$2500	$0.7
Salicylate Color Disc	$90	$3.4
Ammonia Headspace Testing Gas Detection Tube	$700	$5
Nessler Color Disc	$70	$2.4

7.4. Testing Duration

Testing durations for each of the methods are found in Table 25. The salicylate color disc method has the greatest test duration and was considered the least favored method with respect to analysis time. The other methods all has similar test durations that would be appropriate for the testing frequency required of operators.

Table 25. Time Required for Extracting and Analyzing each Sample

Methods	**Calibration Time (min)**	**Analysis Time (min)**
ISE	15	9
Salicylate Color Disc	Not required	30
Ammonia Headspace Testing Gas Detection Tube	1 hr. (Required once)	5
Nessler Color Disc	Not Required	4

Calibration is necessary for the gas tube method and does require a significant amount of preparation time. However, the calibration procedure is only required once as long as the same laboratory equipment is used. Because no recurring calibration is needed, the time necessary for initial calibration is not considered to be prohibitive to the use of the gas tube method.

8. Beta Testing

The goal of the SOP developed in Task 6 was to provide a method that could be used by a variety of industrial end users. Task 7 involved providing a training session demonstrating its use. The end users were provided with several blind samples for analysis and were asked to analyze some of their own samples. In addition, the same samples were tested with the method currently used at the facility to provide a comparison between the current and proposed method. The results of these efforts as well as operators' comments about the proposed method were used to refine the SOP as needed.

One candidate industrial end user was identified in Florida. Arrangements were made to carry out the beta testing tasks at Separation Technologies in Gibsonton, FL. This section of the report describes outcomes of Task 7. The gas tube method SOP described in Task 6 was provided to operators at Separation Technologies to conduct tests on a provided spiked fly ash sample and an ammoniated fly ash product sample from the operator's facility. The ash product is the fly ash that has undergone treatment to remove a fraction of its ammonia content and is being distributed as a cement product. The Nessler colorimetric method, the current method used by the operators at Separation Technologies, was also performed on the same samples as a comparison. Nessler method duration and procedures, as well as operator comments about the SOP (gas tube method), were recorded.

The testing procedure used by operators at Separation Technologies is the Nessler color disc method. Operators weighed a 1.5 g sample of fly ash and added it to 50 mL of water contained in a centrifuge tube. Using a pipette, 0.5 mL of 10 M NaOH was added to the centrifuge tube containing the fly ash slurry. The centrifuge tube was capped and shaken by hand for ten seconds. Using a syringe filter, a 5-mL sample of filtrate was added to a glass vial. One drop of a stabilizing salt solution and three drops of the Nessler's reagent were added to the vial. The vial was shaken and placed in the viewing port of the color disc box. After 1 minute was allowed for color development, the color wheel was rotated to match the resulting color in the test vial. The matched color corresponded to an aqueous concentration and was converted to the concentration of ammonia in the fly ash using software.

Tests using both the Nessler and gas tube method were conducted on a sample of spiked fly ash provided by the research team as well as a sample of fly ash product from the facility. The operator ran six trials on the facility product and three trials on the spiked ash sample using the Nessler method. After a demonstration from the research team, the operator ran two trials on the facility product using the gas tube method and commented on the procedure. Three additional trials on the facility product with the gas tube method were conducted at the UF laboratories by the research team. In addition to testing, information about testing frequency and the existing testing procedure at the facility was gathered in addition to the demonstration of the proposed gas tube method. The beta testing visit was approximately three hours in duration.

The duration of the gas tube method SOP is approximately 5 min, while the duration of the Nessler method being used at the beta test site is approximately 4 min. These method durations are comparable and are both appropriate given the rate of testing observed at Separation Technologies.

Variability between different analysts when reading color wheel results was an issue identified in both the UF laboratories and the beta test site. The maximum observed variation between Nessler color disc readings was 0.2 ppm between three different analysts. This translates to approximately an 8 mg/kg variation in ash ammonia concentration. It was also observed that the 1 minute color development period, as indicated in the HACH Nessler method instructions (HACH Company), was sometimes rushed. Replicate tests on a spiked fly ash showed that when the color development time was more strictly observed, the percent recovery of the expected concentration increased from 84% to 99%.

The gas tube method SOP results were observed to have the smallest relative standard deviation between replicate measurements. The relative standard deviation of the Nessler method results are roughly three times greater than that of the gas tube method for the ash product sample tested. Results from comparative testing on the facility AFA sample are presented in Table 26.

Table 26. Results of Nessler colorimetric method and gas tube method testing on a sample of facility ash product.

Ash Product Ammonia Concentrations	
Nessler Method (ppm ammonia)	Gas Tube Method (ppm ammonia)
64	61
48	68
52	65
60	61
64	61
48	-
Avg. 56	**63**
RSD 14 %	**5 %**

Based on the results of the beta testing, the research team concluded that the gas tube method should remain as the method of preference for FDOT required testing at operational facilities. However, comparison between gas tube SOP and Nessler method results on the facility ash product and spiked fly ash sample do show that the Nessler method provides a relatively robust, and reliable measurement technique for Separation Technologies, and thus is considered an acceptable technique for internal testing.

Comments were provided by the industrial operator conducting the gas tube method SOP. The operator indicated that the duration and simplicity of the gas tube method was similar to that of the Nessler method. The operator also commented on the difficulty of inserting and removing the gas tube from the sampling hole in the rubber stopper and the potential for injury should the gas tube break during handling. This concern will be addressed in the finalized SOP.

9. Finalized Standard Operating Procedure

Information gathered from the beta testing visit described in Task 7 was used to refine the SOP developed in Task 6.

Ammonia Detection Using Sensidyne Gas Detection Pump

1. Scope

1.1. This method is designed for the determination of ammonia concentrations in coal fly ash.

2. Apparatus

2.1. Magnetic stir plate, Fisher Scientific Thermix™ Stirrer Model 120S (or equivalent)

2.2. PTFE coated magnetic stir bar (6.35 cm length)

2.3. 1000 mL borosilicate Erlenmeyer flask

2.4. Two-hole rubber stopper (with 5 mm diameter holes)

2.5. 10, 100, and 500 mL graduated cylinders

2.6. Sensidyne® gas detection pump (Model AP-20S)

2.7. Sensidyne® ammonia gas detector tubes (0.2-20 ppm, 105SD)

2.8. Polystyrene pipette tube (1 mL)

2.9. Parafilm® laboratory film

2.10. Analytical scale (0.0001 g)

2.11. pH indicating paper, pH 10-12 range (or equivalent)

2.12. Three Wide-mouth 2 L HDPE bottle with closure

2.13. Rotary Agitation Apparatus (2-vessel, 3740-2-BRE or equivalent)

2.14 Bench Scale (0.1 g)

2.15. Crystalline Ammonium Sulfate (CAS Number 7783-20-2)

3. Reagents

3.1. 1 N Sodium Hydroxide Solution

4. Calibration

4.1 Preparation of quality control fly ash samples for calibration

In order to appropriately calibrate the system two quality control samples should be prepared. These samples should be produced from dry fly ash samples known to contain no ammonia. To samples will be prepared that contain 50 and 120 mg NH_3/kg-dry ash. Using a bench scale, weigh two 500 g samples of fly ash to the nearest 0.1 g and place each sample into a dry, 2 L wide-mouth HDPE bottle. For the 50 mg NH_3/kg-dry quality control sample, weigh 0.092 g (± 0.0005 g) of powdered ammonium sulfate in a weigh boat using an analytical scale and add carefully to one of the 2 L bottles containing fly ash. For the 120 mg NH_3/kg-dry quality control sample, weigh 0.220 g (± 0.0005 g) of powered ammonium sulfate in a weigh boat using an analytical scale and add carefully to the second 2 L bottle containing fly ash. Ammonium sulfate should be pulverized in a mortar and pestle until at least 90% of the ammonium sulfate salt is passing a 100 mesh sieve. Close both bottles and place them on a rotary agitator for 30 minutes between 10-40 rpm.

4.2 Development of calibration curve

Follow the procedure in section 5 to measure the concentration of ammonia in quality control fly ash samples. Plot the adjusted tube readings against the corresponding fly ash concentration (50 and 120 mg NH_3/kg-dry ash) to develop a calibration curve specific to the equipment used. Use the equation of the least squares regression line fit to the calibration data to convert tube readings (in parts-per-million by volume) to ammonia concentrations in the fly ash as mg-NH_3/kg AFA. A sample calculation is provided in Section 6.

4.3 Alternative preparation of quality control samples with ammoniated fly ash for calibration

If ammonia-free fly ash is not available, obtain a >1.5 kg sample of dry, ammoniated fly ash. Weigh three, 500 g samples of ammoniated fly ash to the nearest 0.1 g using a scale and place each sample into three 2 L HDPE bottles. For two of the three samples, follow the procedure described in Section 4.1 to create both quality control ash samples for calibration (50 and 120 mg NH_3/kg-dry ash). Also place the third sample (containing no added ammonium sulfate) on the rotary agitator as described in Section 4.1. Follow the procedure in Section 5 to determine the detection tube reading for the sample with no added ammonium sulfate salt; this will provide a background reading. If sample ammonia concentrations exceed the range of the detection tubes, the pump operation can be modified to adjust the volume of headspace gas sampled (see Sensidyne manual) or higher range detection tubes could be used. Follow the procedure in Section 5 to obtain tube readings for the two quality control samples. Subtract the background tube reading from the quality control sample tube readings. Plot the difference (corrected headspace tube readings) against the corresponding fly ash concentration (50 and 120 mg NH_3/kg-dry ash) to develop a calibration curve specific to the equipment used. Use the equation of the least squares regression line fit to the calibration data to convert tube readings (in parts-per-million by volume) to ammonia concentrations in the fly ash as mg-NH_3/kg AFA. A sample calculation is provided in Section 6.

4.4 Alternative Method without Calibration

While the calibration method described in Section 4 is preferred for improving the accuracy of measurements, an alternative method not requiring calibration can be used if development of a calibration curve with spiked fly ash samples is not feasible.

The use of this alternative method requires that the 1000 mL Erlenmeyer flask have a total volume of 1,095 ± 10 mL with the stopper in order to be used for the headspace gas tube testing procedure. To determine the volume of a flask, carefully fill the flask with water until the bottom of the stopper touches the water surface when inserted into the flask opening. Using a 500 mL graduated cylinder, measure and record the volume of water contained in the flask to the nearest 5 mL. Ensure that no water is spilled when transferring water from the flask to the graduated cylinder. This volume must be 1,095 ± 10 mL in order for the flask to be used without a calibration procedure.

5. Procedure

5.1 Obtain a dry representative sample of fly ash collected according to ASTM C702, Standard Practice for Reducing Samples of Aggregate to Testing Size.

5.2 Using an analytical balance, weigh 10 g of fly ash sample to the nearest 0.01 g in a weigh boat.

5.3 Measure 10-mL (±1 mL) of 1 N sodium hydroxide solution in a 10-mL graduated cylinder.

5.4 Add 100 mL of de-ionized water to a clean 1000-mL Erlenmeyer flask containing a 6.35-cm PTFE-coated magnetic stir bar.

5.5 Insert a 1 mL polystyrene pipette tube through one of the stopper holes so that the tip of the pipette extends roughly halfway into the 1000 mL Erlenmeyer flask when the stopper is on. Ensure that the opening size of the second sampling hole is sufficiently large to allow easy and safe insertion/removal of gas tubes. The sampling hole should also be small enough so that a seal is made around the gas tube, preventing the escape of gases. Moistening the outside of the tube with a damp cloth is recommended if insertion/removal of the tube becomes difficult. Cover the second hole with Parafilm until it is time to insert the gas tube.

5.6 Place Erlenmeyer flask on the stir plate and adjust the speed of the stir bar to be approximately between 90 and 130 rpm to allow sufficient stirring without sloshing.

5.6 While stirring, add the 10 g sample of fly ash into the Erlenmeyer flask and stopper the flask. Allow slurry to mix for one minute.

5.7 During the one-minute period, break off both tips of the Sensidyne detection gas tube in the tip cutter on the gas tube pump (see manufacturer’s instructions manual).

5.8 At the end of the one minute period, add 10 mL of 1 N sodium hydroxide and immediately stopper the flask with the two-hole stopper prepared in step 5.5. Allow the slurry to mix for one minute, then stop stirring.

5.9 Insert the detection tube carefully and tightly into the pump following the manufacturer's instructions (making sure that the arrow on the tube points toward the pump). Remove the Parafilm from the stopper hole and insert the detection tube through the stopper hole so that approximately 1 inch of the tube extends into the flask headspace.

5.9 Measure the gaseous ammonia concentration in the flask headspace according to the Sensidyne gas detection pump instructions. Ensure that the stopper is not removed from the flask or the tube removed from the stopper while sampling.

5.10 Test the pH of the slurry and verify that it exceeds 12.0. If pH is below 12, repeat procedure using 12 mL instead of 10 mL of NaOH solution (Step 5.8).

5.11 Record the value read from the detection tube and calculate the ammonia concentration in the fly ash using the appropriate method (see Section 4.3 and Section 6).

6. Calculation

6.1 Use the equation of the least squares regression line fit to the calibration data to convert tube readings to ammonia concentrations in mg-NH_3/kg AFA. A sample calculation is provided.

Sample Calculation:

Example equation of the least squares regression line: $y = 0.068x - 0.34$ Eq. 6.1a

Where y = gas tube reading and x = ammonia concentration in fly ash sample

$$\frac{(\text{Tube Reading}) + 0.34}{0.068} = \text{Ash Concentration } (\text{mg} - \text{NH}_3/\text{kg AFA}) \qquad \text{Eq. 6.1b}$$

$$\frac{(4.0) + 0.34}{0.068} = 64 \ \text{mg} - \text{NH}_3/\text{kg AFA} \qquad \text{Eq. 6.1c}$$

6.2 If the alternative method without calibration was used, multiply the gas tube ppm reading by 15.2 to yield the concentration of ammonia in the fly ash sample (mg-NH_3/kg AFA).

7. Sample Holding and Preservation

7.1 If fly ash samples will not be tested immediately, samples should be kept in a dry, sealed HDPE bottle. Samples kept in this condition have a holding time of two weeks. Minimizing the time that the container is open is recommended for sample preservation.

7.2 Spiked fly ash samples used for calibration shall be used within 3 days after preparation.

8. Precision and Quality Control

8.1 Measurements shall be conducted in triplicate for the development of the calibration curve. The percent relative standard deviation (%RSD) between replicate measurements should be below 20%. Calibration should be repeated if the %RSD exceeds this value. The %RSD calculation is described in Equation 8.1.

$$\% RSD = \frac{Sample\ Standard\ Deviation}{Sample\ Mean}(100) \qquad \text{Eq. 8.1}$$

10. Summary and Recommendations

Based on the data and observations, the headspace gas detection tube method is recommended as a preferred test procedure because of higher accuracy and precision, appropriate test duration, and practical running costs. The gas detection tube method is also considered to be a more robust procedure as it does not involve an extraction procedure and is much less susceptible to interferences more commonly observed with aqueous analysis. Unlike the colorimetric methods where readings for the same sample would vary between analysts, minimal variability for gas tube readings was observed. This was attributed to the well-defined color change “front” produced within the tube that is measured against the tube graduations. After developing a calibration curve for the gas tube method equipment, results remained consistent. This was favored over the frequent calibration and probe care needed for ion-selective electrode analysis.

A derivative of the gas detection tube method is used by Headwaters Resources, one the nation’s leading ash suppliers who handles the assay for ash management within the Southern Company. During beta testing, operators at Separation Technologies considered the gas tube method to have similar ease of use and test duration compared to the Nessler method currently used at the facility. While the results from beta testing demonstrated that the Nessler colorimetric method does provide a relatively robust and reliable measurement technique for Separation Technologies, the gas tube method will be recommended to the DOT and industrial end-users as it provides the desired accuracy and precision as well as an alternative method that does not involve the use and disposal of hazardous reagents.

11. References

American Coal Ash Association, (2012). *2012 Coal Combustion Product Production & Use Survey*. American Coal Ash Association, Lexington, KY.

American Society of Testing and Materials, (2010). *Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass*. ASTM International, West Conshohocken, PA.

Adepetu, J.A., Nabhan, H., Osinubi, A. (1996). “Simple Soil, Water and Plant Testing Techniques for Soil Resource Management”. *Proc. Train. Course Held Ib. Niger.* 16–27.

Ban, H. (2001). “Ammonia/Fly Ash Interactions”, EPRI, Palo Alto, CA: 1008310.

Brendel, G.F., Bonetti, J.E., Rathbone, R.F., Frey Jr., R.N. (2000). “Investigation of Ammonia Adsorption on Fly Ash due to Installation of Selective Catalytic Reduction Systems”. Office of Scientific & Technical Information (No. 834465). U.S. Department of Energy.

Bower, C.E., Bidwell, J.P. (1978). “Ionization of Ammonia in Seawater: Effects of Temperature, pH, and Salinity”. *J. Fish. Board Can.* 35, 1012–1016.

Cannon, J., Cushing, K. (2005). “Ammonia/Fly Ash Interactions” (No. 1008310), EPRI, Palo Alto, CA.

Cardone, C., Kim, A., Schroeder, K. (2005). “Release of Ammonia from SCR/SNCR Fly Ashes.” *2005 World of Coal Ash Conference*. Lexington, KY: World of Coal Ash.

Cushing, K., Hinton, S. (2004). “Short-Term Variability of Ammonia in Fly Ash” (No. 1008309), EPRI, Palo Alto, CA.

Eaton, A.D., Franson, M.A. (2012). “Standard Methods for the Examination of Water and Wastewater”. American Public Health Association, Washington, D.C.

Emerson, K., Russo, R.C., Lund, R.E., Thurston, R.V. (1975). “Aqueous Ammonia Equilibrium Calculations: Effect of pH and Temperature”. *J. Fish. Board Can.* 32, 2379–2383.

Florida Department of Environmental Protection. (2009). *Florida DEP Comments – Part II (Docket ID Number OAR-2002-0051).* Florida Department of Environmental Protection, Tallahassee, FL.

Golden, D.M. (2001). “Impacts of Ammonia Contamination of Fly Ash on Disposal and Use”. EPRI, Palo Alto, CA: 1004609.

HACH Company, Nitrogen Ammonia Test Kit Manual, Model NI-8, Color Disc Kit 2241-00.

Hayes, J. B. (2013). *Investigation of Ammonia and Trace Elements Leaching from Cement and Concrete Products Amended with Cement Kiln and Coal Boiler Combustion By-Products* (Master’s Thesis, University of Florida).

Hinton, W.S., Cushing, K.M., Heaphy, R.F., Rubel, A. (2002). “Behavior of Ammoniated Fly Ash: Effects of Ammonia on Fly Ash Handling, Disposal, and End- Use”. EPRI, Palo Alto, CA: 1003981.

Keeney, D.R., Nelson, D.W. (1982). “Nitrogen—Inorganic Forms”. *Methods Soil Anal. Part 2 Chem. Microbiol. Prop.* 643–698.

Kempers, A.J., Zweers, A. (1986). “Ammonium Determination in Soil Extracts by the Salicylate Method”. *Commun. Soil Sci. Plant Anal.* 17, 715–723.

Knepel, K. (2003). “Determination of Nitrate in 2 M KCl Soil Extracts by Flow Injection Analysis”. *QuikChem Method 12,* 107–04.

Kosson, D.S., Sanchez, F., Kariher, P., Turner, L.H., Delapp, R., Seignette, P. (2009). “Characterization of Coal Combustion Residues from Electric Utilities–Leaching and Characterization Data”. United States Environmental Protection Agency EPA-600R-09151.

Kozloski, G.V. Senger, C.C.D., Perottoni, J., Sanchez, L.M.B., (2006). “Evaluation of Two Methods for Ammonia Extraction and Analysis in Silage Samples”. *Anim. Feed Sci. Technol.* 127, 336–342.

Li, L., Zhang, J., Xing, W., Chen, W., Wu, X., Zhu, K. (2006). “Development and Validation of a New Soil Universal Extractant: 0.02 Molar Strontium Chloride”. *Commun. Soil Sci. Plant Anal.* 37, 1627–1638.

Mehta et. al. (2004). “Dry and Semi-dry Methods for Removal of Ammonia from Fly Ash”. U.S. Patent US 6746654 B2.

Palumbo, A.V., Tarver, J.R., Fagan, L.A., McNeilly, M.S., Ruther, R., Fisher, L.S., Amonette, J.E. (2007). “Comparing Metal Leaching and Toxicity from High pH, Low pH, and High Ammonia Fly Ash”. *Fuel* 86, 1623–1630.

Rathbone, R.F., Robl, T.L. (2001). “A Study of the Effects of Post-Combustion Ammonia Injection on Fly Ash Quality: Characterization of Ammonia Release from Concrete and Mortars Containing Fly Ash as a Pozzolanic Admixture”. United States Department of Energy. Washington, D.C.

Schert, J., Townsend, T., Wu, C.-Y. (2012). “Identification of Potential Concerns Associated with FDOT Use of Ammoniated Fly Ash (No. BDK75 977-43)”. Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL.

Switala, K. (1993). “Ammonia (salicylate) in 2 M KCl Soil Extracts”. *QuikChem Method 12*, 107–06.

Tel, D.A., Heseltine, C. (1990). “The Analyses of KCl Soil Extracts for Nitrate, Nitrite and Ammonium Using a TRAACS 800 Analyzer”. *Commun. Soil Sci. Plant Anal.* 21, 1681–1688.

Thermo Scientific, (2007). *User Guide, High Performance Ammonia Ion Selective Electrode.*

Thurston, R.V., Russo, R.C., Emerson, K. (1977). *Aqueous Ammonia Equilibrium Calculations*, (Technical Report No. 74-1). Fisheries Bioassay Laboratory, Montana State University, Bozeman MT.

United States Department of Transportation. (2011). *Fly Ash* [WWW Document]. US Dep. Transp. Fed. High Way Adm. URL http://www.fhwa.dot.gov/infrastructure/materialsgrp/flyash.htm (accessed 1.30.14).

United States Environmental Protection Agency. (2011). *EPA Materials Characterization Paper: Final Rulemaking: Identification of Nonhazardous Secondary Materials That Are Solid Waste Coal Combustion Residuals - Coal Fly Ash, Bottom Ash, and Boiler Slag.* (Collections & Lists). United States Environmental Protection Agency, Washington, DC.

Wang, H., Ban, H., Golden, D., Ladwig, K. (2002). “Ammonia Release Characteristics From Coal Combustion Fly Ash”. *Abs Paps Am Chem Soc Div Fuel Chem* 47, 836–838.

Wang, J., Wang, T., Mallhi, H., Liu, Y., Ban, H., Ladwig, K. (2007). “The Role of Ammonia on Mercury Leaching from Coal Fly Ash”. *Chemosphere* 69, 1586–1592.