

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

Semi-Annual Technical Progress Report
for the Period 08/11/00 to 04/11/01

Principal Authors:

Robert F. Rathbone and Thomas L. Robl
University of Kentucky Center for Applied Energy Research
2540 Research Park Drive
Lexington, Kentucky 40511-8410

on behalf of:

University of Kentucky Research Foundation
201 Kinkead Hall
Lexington, KY 40506

U.S. DoE Cooperative Agreement Number: DE-FC26-00NT40908

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

Work completed in this reporting period focused on finalization of the Work and Management Plan, sample acquisition and analysis, evaluation of ammonia measurement methods, and measurement of ammonia loss from mortar. All fly ash samples have been acquired and analyzed for chemical composition and particle fineness. Three non-ammoniated fly ash samples were obtained from power plants that do not inject ammonia for NO_x or particulate control, whilst three ammoniated fly ashes originate from plants that inject ammonia into the flue gas. The fly ash sources were selected based on their marketability as concrete admixtures and ammonia content. Coarse and fine aggregates for mortar and concrete testing have also been secured and have been thoroughly characterized using ASTM methods. Methodologies for the measurement of ammonia in the gaseous and aqueous phase have been carefully considered in the context of their suitability for use in this project. These include ammonia detection tubes, carbon impregnated with sulfuric acid (CISA) tubes, titration, and electrochemical methods. It was concluded that each of these methods is potentially useful for different aspects of the project, depending on the phase and concentration of ammonia to be measured. Preparation of fly ash-containing mortars both with and without ammonia indicated that the ammonia has no significant influence on compressive strength. Finally, measurement of ammonia loss from mortar has begun and the results of several of these experiments are included herein. It has been found that, under the laboratory curing conditions devised, ammonia release from mortar occurs at a relatively rapid rate in the first 24 hours, proceeded by a much slower, essentially linear rate. Furthermore, at the end of the three-week experiments, it was calculated that greater than 80% of the initial ammonia concentration remained within the mortar.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	6
EXPERIMENTAL	7
A. Materials Sampling and Testing	7
A.1. Fly Ash	7
A.2. Aggregates	7
B. Mortar Mixing	7
C. Unconfined Compressive Strength (UCS) of Mortars	8
D. Evaluation of Ammonia Measurement Techniques	8
Detection Tubes	8
CISA Tubes	9
Ammonia Capture in Acidic Solution	9
E. Ammonia Loss from Mortar	10
E.1. Effects of Ammonium Salt Type	10
E.2. Ammonia Loss Rate	11
RESULTS AND DISCUSSION	12
A. Unconfined Compressive Strength	12
B. Ammonia Loss from Mortar	12
B.1. Effect of Salt Type	12
B.2. Effect of Water:Cementitious Ratio	12
CONCLUSIONS	13
REFERENCES	14

LIST OF TABLES

Table 1. Source and General Information for Fly Ash Samples	16
Table 2. ASTM C 618 Data for Fly Ash Samples	16
Table 3. Chemical Composition of Fly Ash Samples	17
Table 4. Aggregate Testing Data	17
Table 5. Mortar Mix Proportions	17
Table 6. Test of Ammonia Trapping Experimental Set-Up	18
Table 7. Unconfined Compressive Strength of Mortar	18
Table 8. Unconfined Compressive Strength of Mortar with Added Ammonia	18

LIST OF FIGURES

Figure 1. Laboratory mixer used to prepare mortar.	19
Figure 2. Equilibrium gaseous ammonia measurements using Sensidyne and GasTec detection tubes.	20
Figure 3. Experimental apparatus used for the measurement of the rate of ammonia loss from mortar.	21
Figure 4. The effect of ammonium salt type on ammonia loss from mortar.	22
Figure 5. Effect of W:C ratio on ammonia loss from mortar: Rockport fly ash. . . .	23
Figure 6. Effect of W:C ratio on ammonia loss from mortar: Bowen fly ash.	24

EXECUTIVE SUMMARY

Work completed in this reporting period focused on finalization of the Work and Management Plan, sample acquisition and analysis, evaluation of ammonia measurement methods, and measurement of ammonia loss from mortar. All fly ash samples have been acquired and analyzed for chemical composition and particle fineness. Three non-ammoniated fly ash samples were collected from power plants that do not inject ammonia for NO_x or particulate control. These samples represent fly ash that are marketed as concrete pozzolanic admixtures, that is, they possess suitable fineness, carbon content, chemical composition, and strength index. In addition, three fly ash samples originated from plants that inject ammonia into the flue gas for fly ash conditioning. These fly ash sources were selected based on their marketability as concrete admixtures as well as their ammonia content. Each fly ash was collected and stored in tightly closed 55 gallon drums.

Coarse and fine aggregates for mortar and concrete testing have been secured and have been characterized using ASTM methods. Approximately 5 tons of coarse aggregate and 3 tons of fine aggregates were acquired and stored in a fully enclosed materials storage bay. The aggregates pass ASTM specifications for particle size distribution, specific gravity, water absorption, and bulk density. These data will be utilized for concrete mix proportioning. The necessary equipment for preparation and testing of mortar and concrete have been purchased.

Methodologies for the measurement of ammonia in the gaseous and aqueous phase have been carefully considered in the context of their suitability for use in this project. These include ammonia detection tubes, carbon impregnated with sulfuric acid (CISA) tubes, titration, and electrochemical methods. It was concluded that each of these methods is potentially useful for different aspects of the project, depending on the phase and concentration of ammonia to be measured. However, the CISA tubes were ruled out because of their low adsorption capacity and lack of an indicator. Instead, an electrochemical technique is being developed for absorption and measurement of ammonia that has been released from mortar, whilst ammonia detection tubes provide a rapid, accurate "spot measurement" of ammonia entrapped in an enclosed space over a mortar slab.

Preparation of fly ash-containing mortars both with and without ammonia for the purpose of compressive strength testing have been completed. The tests indicated that ammonia has no significant influence on compressive strength, even at a high ammonia concentration (200 mg N/kg ash). The type of ammonium salt added to the mortar mix also has no significant effect on the ammonia loss from mortar.

Finally, measurement of ammonia loss from mortar has begun and the results of several of these experiments are included herein. These experiments utilize 15.2 cm X 30.5 cm (6 in. X 12 in.) cylinders containing damp sand as a substrate, a mortar layer, and a 1 L space above the mortar. Air is flowed through the space and passed through an acetic acid trap. Ammonium ion is periodically measured in the acetic acid and the quantity lost from the mortar calculated. It has been found that, under the laboratory curing

conditions devised, ammonia release from mortar occurred in two stages: a rapid exponential decrease in ammonia concentration, followed by a much slower, nearly linear decrease. After 3 weeks (the duration of the experiments) most of the ammonia remained entrapped within the hardened mortar. However, ammonia continued to diffuse out of the mortar, at a slow rate, over longer time periods. Furthermore, water:cementitious ratio exerts a significant influence on ammonia loss rate from mortar, with a higher W:C ratio causing a higher loss rate. This is likely due to a higher degree of porosity, and thus greater diffusivity, within the wetter material.

EXPERIMENTAL

A. Materials Sampling and Testing

A.1. Fly Ash

Samples of fly ash were acquired from six different power plants. Three of these samples were collected by CAER staff, whilst the remaining three were collected by plant staff and shipped to the CAER. Approximately three 208 L (55 gal.) drums of each ash were obtained, and were tightly sealed and stored in an enclosed facility. The fly ash sources were selected based on ash quality (e.g. fineness, carbon content) and ammonia content. The sources and general properties of the fly ashes are provided in Table 1, ASTM C 618 requirements in Table 2, and chemical composition is provided in Table 3. The data indicate that seven of the fly ashes are suitable for use in concrete as a pozzolanic admixture, whereas the Yates sample contains an excessive amount of carbon and thus does not pass ASTM C 618 requirements (max. 6% LOI). However, the relatively high ammonia content of this ash makes it desirable for studying ammonia loss from mortar and concrete. The chemical composition of each ash is reflective of the feed coal: Rockport contains a relatively high content of alkali and alkaline-earth elements, while Mill Creek and Conesville contain comparatively large amounts of iron, indicative of the high-sulfur (e.g. pyrite) northern Appalachian feed coal.

The ammonia content of the ammoniated fly ash samples was measured by mixing 50 g of fly ash with 150 ml distilled water in a polyethylene bottle. The mixtures were shaken periodically for approximately 48 hours, whereupon the solution was filtered. The pH of the filtrate was adjusted to greater than 11.5, and the ammonia content measured using an Orion 95-12 NH₃ electrode. The quantity of water soluble ammonia present on the ash was then calculated.

A.2. Aggregates

Aggregates for mortar and concrete testing were acquired during this reporting period. As is described below, ASTM graded standard sand was utilized in the mortar experiments, and thus was not characterized further. In contrast, the coarse and fine aggregates to be used in the concrete experiments were characterized in accordance with ASTM C 29, C 70, C 127, C128, C 136, C 566, and D 75. A summary of these data are presented in Table 4. Approximately 5 tons of the coarse aggregate (ASTM designation "57") and 3 tons of the fine aggregate (sand) were obtained and stored in an enclosed facility.

B. Mortar Mixing

Mortar samples were mixed in accordance with ASTM C 305, using a Hobart mixer (Figure 1). Two mixes were designed to represent a fairly wide range of water:cementitious (cement + fly ash) ratio. The “Low W:C Mix” was proportioned to meet ASTM C 109 specifications for a “standard mortar”, whereas the “High W:C Mix” comprises a similar cement + fly ash:sand ratio, but a higher proportion of water (Table 5). All mortars in this study were prepared using ordinary Portland cement (OPC), fly ash, distilled water, and ASTM standard sand. Initially, a third mix (“UCS Mix”; Table 5) was designed and utilized for the compressive strength testing of mortar. However, after completion of the testing the project group members decided that the standard ASTM mortar mix would be more suitable for the remaining work in the project. Therefore, unconfined compressive strength data was obtained using the “UCS Mix” mortar, whereas ammonia release studies used the other two mixes.

Ammonia was added to mortars prepared with non-ammoniated fly ash by completely dissolving ammonium sulfate in the mix water, at a specified concentration, before the water was mixed with the OPC and sand. No additional ammonia was added to mortars containing ammoniated fly ash. During mixing of mortars containing either added ammonia or ammoniated fly ash, the space between the top of the mixing bowl and the mixer head was enclosed using a flexible plastic sheet (i.e. a large plastic bag with the end cut off) that was sealed to the bowl and mixer using a rubber band. This set-up was utilized to minimize ammonia loss during mixing.

C. Unconfined Compressive Strength (UCS) of Mortars

After mixing, mortar samples were prepared for UCS testing by casting into cube molds (5.1 cm X 5.1 cm X 5.1 cm) in accordance with ASTM C 109. The only significant deviation from ASTM specifications was the use of plastic molds instead of metal. The mortar cubes were placed into polyethylene bags containing a wet paper towel, sealed, and cured for 24 hrs. After this initial set, the samples were transferred to a humidity- and temperature-controlled curing room at Gregg Laboratory, Lexington, KY. UCS data were acquired after 7 days and 28 days curing at Gregg Laboratory.

D. Evaluation of Ammonia Measurement Techniques

Several techniques were evaluated for measuring ammonia that has off-gassed from mortar. These techniques are divided into two main groups: those that capture the ammonia on a solid sorbent within a glass tube, and those that trap the ammonia in an aqueous acid solution.

Detection Tubes

Ammonia detection tubes, containing a solid sorbent with indicator are useful for “spot-sampling” air in the workplace and provide an accurate, repeatable measurement although the sampling volume is very small (typically 100 cm³). These tubes utilize an air sampling syringe that pulls a specific volume of air through the tube at a specific rate and the ammonia concentration in the air is read directly on the tube by observing a color change in the sorbent.

In this study, several brands of the detection tubes were evaluated for their ability to

accurately measure ammonia that has been released from mortar into an enclosed, overlying space ("head-space"). To accomplish this, 200 ml of aqueous ammonia solutions were prepared using several different ammonium salts and sodium hydroxide and sealed in 1 L polyethylene bottles. The solutions were periodically shaken in the bottles for 15 minutes, whereupon 100 cm³ of air was sampled through the detection tube. A similar procedure was followed for freshly mixed mortar containing ammonia added as ammonium sulfate. Figure 2 graphically illustrates that the detection tubes provide a precise measurement of gaseous ammonia in equilibrium with a solution, even when the aqueous solution is a component of mortar. In the latter case, two mortar mixes were prepared as described above, at two different ammonia concentrations, and the equilibrium ammonia concentration in the head-space measured using the same technique as for the aqueous solutions. It was evident that the data points obtained from the mortar lie on the same line as those from the solutions (Figure 2). It was also evident that at high ammonia concentrations (e.g. greater than 100 mg/L) the different brands of tubes produce significantly different readings.

CISA Tubes

Carbon Impregnated with Sulfuric Acid (CISA) tubes are currently recommended by NIOSH and OSHA for accurate sampling for ammonia in the workplace (NIOSH 6015 and 6016, and OSHA ID-188). In this method, a larger volume of air (up to 24 L) is pulled through the CISA tube for a specified time using a sampling pump. Ammonia in the air is sorbed onto the CISA beads as ammonium sulfate. The CISA beads are then removed from the tube, extracted with distilled water, and the ammonium ion measured in solution using ion chromatography. This method replaces an earlier one in which ammonia is bubbled through and trapped in dilute sulfuric acid, and the ammonia concentration determined by titration. The CISA tubes (purchased from Supelco, Inc.) were considered for use in this project, but were determined to be unsuitable for several reasons. The maximum air flow that is recommended to be passed through the tubes is 0.5 L/min, which is less than what is required for our experiments, particularly the larger-scale concrete tests. Another drawback was the relatively small adsorption capacity of approximately 2 mg ammonia before break-through occurred. This small capacity, combined with the lack of an ammonia concentration indicator within the CISA beads requires that the tubes be replaced at frequent intervals over the course of an experiment. Therefore, it was concluded that CISA tubes would not be used for the project.

Ammonia Capture in Acidic Solution

Based on the testing of the CISA tubes, it was decided to utilize an aqueous acid solution to trap ammonia as it is released from mortar and concrete. Prior to utilization of the CISA tube method, OSHA recommended an ammonia measurement procedure (OSHA Method ID 164) in which a sample of air is bubbled through a sulfuric acid trap, and the ammonium ion measured in solution. A similar methodology exists for measurement of ammonia in ammonium salts, wherein the salts are dissolved in an aqueous sodium hydroxide solution and the solution distilled. The ammonia vapor distillate is trapped in either sulfuric acid or boric acid and the ammonia concentration determined by titration (Labconco, 2001). The boric acid technique has recently been

applied in the study of ammonia evolution from concrete during mixing (Majors and Rathbone, 2001).

The measurement of ammonia in aqueous solution can be accomplished using various techniques. These include, titration, colorimetric, enzymatic, and electrochemical methods. It is beyond the scope of this report to discuss each of these in detail, therefore, the reader is referred to an excellent (although somewhat dated) review by Richards (1984). Based on a review of the different methods, an electrochemical method was selected for this project to measure ammonia loss from mortar. This method employs a magnesium acetate - acetic acid buffer (0.1 ionic strength) to trap evolved ammonia, combined with an Orion Model 93-18 ammonium ion-specific electrode (ISE) to measure the ammonium concentration of the “trap solution”. Although the ammonium electrode in traditional use suffers interferences from other monovalent cations in solution, in this application the only cations present apart from ammonium (NH_4^+) are hydronium (H_3O^+) and magnesium (Mg^{2+}), which produce negligible interference at the 0.1 ionic strength and pH (4.74) of the trap solution. Furthermore, calibration of the ammonium electrode is accomplished using the same solution as the trap solution (described in the Orion electrode manual).

The stability of ammonium ion in the trap solution was evaluated prior to mortar testing, to ensure that the concentration did not decrease with time. To accomplish this, 250 ml of a 10 mg/L ammonia (as N) trap solution was placed in a stoppered Erlenmeyer flask containing a fritted glass bubbler. A 1 L/min air flow (from the laboratory compressed air supply) was passed through the solution over the course of two weeks, and the ammonium concentration periodically measured. After 14 days, the ammonium concentration, as determined using the Orion ISE, remained between 10-11 mg/L. This test also showed that the laboratory compressed air supply contained negligible ammonia contamination.

The accuracy of the experimental method was assessed by preparing 250ml of a 200 mg/L ammonia as N “source” solution (with added NaOH), and bubbling 1 L/min air through the solution. The air stream was then bubbled through 250 ml of trap solution, followed by bubbling through a second trap solution. After 24 hrs, the ammonia remaining in the “source” solution was measured using the Orion gas-sensing electrode, whilst ammonia remaining in the trap solutions was measured using the ammonium ISE. Table 6 provides a summary of the results and indicates that the technique provides an accurate measurement of ammonia lost from a basic solution, and that an insignificant quantity of ammonia escapes the first trap flask (at the 1 L/min flow rate). Thus, it was concluded that the technique is suitable for the mortar experiments.

E. Ammonia Loss from Mortar

E.1. Effects of Ammonium Salt Type

The effect of salt type on ammonia loss from mortar was evaluated using the low W:C ratio mortar, prepared in 2 L batches as described above. Ammonia was added by dissolving ammonium chloride, ammonium sulfate, or ammonium bisulfate in the mix water at a concentration of 100 mg/L as N. Immediately after mixing, the mortar was

placed into a 15.2 cm (6 in.) diameter by 30.5 cm (12 in.) long plastic cylinder that contained 2.5 L of damp Ottawa sand at the base. The wet mortar was rodded 30 times, the surface smoothed with a rubber spatula, and the cylinder sealed using a plastic “snap” lid fitted with a corked two-hole rubber stopper. At specified intervals, the ammonia concentration in the 1 L head-space was measured using a Sensidyne ammonia detection tube. After each measurement, the plastic lid was removed to permit ammonia to be lost to the atmosphere. Prior to the next reading, the plastic lid was snapped back into place and the next ammonia measurement acquired ten minutes after the cylinder was sealed. This procedure was repeated over the course of approximately 20 hrs. Although the methodology did not produce a quantitative measure of the total ammonia lost from the mortars, it did provide a useful comparison between the different ammonium salts.

E.2. Ammonia Loss Rate

Based on ammonia measurement technique testing described above, an experimental set-up was devised for the measurement of ammonia loss from mortar. Two holes were pre-drilled into the sides of a cylinder, near the top edge, and fitted with tight-fitting rubber grommets through which a 1 L/min flow of air was passed into and out of the cylinder head-space (Figure 3). Before entering the cylinder, the air was passed through a bed of CISA beads to remove any ammonia, then through a flask containing distilled water to humidify the air. The effluent (containing ammonia from the mortar) was passed through a diffuser that was placed into a 250 ml Erlenmeyer flask containing the magnesium acetate-acetic acid trap solution (Figure 3).

The trap solution was periodically sampled during the experiment, using a plastic syringe, and the ammonium concentration measured using an Orion ammonium ISE. Upon completion of the measurement, the sample solution was returned to the Erlenmeyer flask. This method permitted the ammonia to accumulate in the trap solution over the course of the experiment since the ammonium electrode technique is non-destructive. Evaporation of the trap solution was compensated for by recording the initial weight of the flask + solution and adding fresh solution each day in sufficient quantity to return the flask to the initial weight.

A flow rate of 1 L/min was chosen because it would approximate conditions found in a closed room with poor circulation, such as those encountered during placement of a concrete slab in an unfinished basement. The rationale for the selection of this flow rate is based on the requirements for outdoor air circulation in a residential living area (ASHRAE 62-1999). The standard requires a ventilation rate of 15 ft³/min/person (425 L/min/person) for an occupied living space. For example, a basement room size of 4.6 m X 4.6 m X 2.4 m high will have a volume of 50,970 L. If the circulation rate is calculated for 5 persons, then the total rate is 2125 L/min. Our laboratory experimental design represents a cylindrical segment of the room that is 15.24 cm in diameter X 2.4 m high, with a volume above the slab of 44.5 L. It follows that the air flow for the cylinder of air is 1.9 L/min, in a properly ventilated living space. However, these conditions will not always be encountered in an unfinished building during construction. Therefore, a more conservative air flow rate of 1 L/min was chosen for our mortar

experiments to represent less than optimum circulation. However, it should be noted that this is only a rough representation of actual circulation conditions. The 425 L/min/person standard considers only CO₂ levels from exhalation; ASHRAE requires additional measures if other contaminants, such as ammonia, are present. Accordingly, the effect of different flow rates on ammonia loss from mortar and concrete will be examined in future experiments.

RESULTS AND DISCUSSION

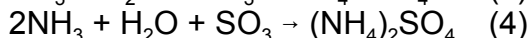
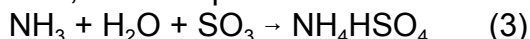
A. Unconfined Compressive Strength

Table 7 presents the results of the unconfined compressive strength (UCS) testing for mortar prepared using the different fly ash samples. The data indicate that all of the fly ashes tested pass ASTM C 618 in the context of strength index (minimum 80% of control strength after 7 days). It is evident from Tables 7 and 8 that the presence of ammonia has no discernible effect on strength. This result is not unexpected since workers have reported for a number of years that ammonia seems to have no negative impact on concrete strength (e.g. Golden, 2001).

B. Ammonia Loss from Mortar

B.1. Effect of Salt Type

In general, the type of ammonium salt added to mortar had no significant effect on ammonia odor emanating from the mortar, or on the loss rate. This is shown graphically in Figure 4. These data are of interest because the primary mechanism for ammonia deposition on fly ash is believed to be the precipitation of ammonium salts on the ash surfaces. Reaction of ammonia with other flue gases, particularly SO₃ and water vapor, causes deposition of ammonium salts on fly ash as well as on the ash collection systems and other components, for example:



Analysis of the deposits found on various types of equipment, such as air heaters, baghouse filters, etc., have confirmed the existence of ammonium sulfate, bisulfate, and sulfite (e.g. Jordan and Casper, 1995). Ammonium chloride is also possible in minor amounts. However, results of this study indicate that the type of ammonium salt(s) present on the fly ash has little effect on ammonia out-gassing from mortar.

B.2. Effect of Water:Cementitious Ratio

The potential influence of water:cementitious (W:C) ratio on ammonia loss rate from mortar has been examined thus far for two fly ash samples. In these experiments, mortar was prepared as described in the Experimental Section. Ammonia was added to the mix water at a concentration of 165 mg N/L solution for both W:C ratio mortars. This provides the equivalent of 400 mg ammonia (as N) per kg of fly ash for the low W:C ratio mortar, and 545 mg ammonia per kg of fly ash for the high W:C ratio mix. The ammonia concentrations were adjusted in this manner to keep the concentration constant on a solution basis, rather than on an ash basis. This procedure enabled the ammonia loss data for the two mortars to be interpreted in the context of W:C ratio only, by making the solution concentration a constant. However, in practice for a single ammoniated fly ash being used in concrete, the ammonia concentration will be higher

for a low W:C mix than in a high W:C ratio mix mainly because a higher proportion of water is added to the latter, thus diluting the ammonia solution concentration. However, the effects of ammonia concentration will be examined in later experiments.

Experiments completed thus far indicate that the overall ammonia loss rate is slightly greater for the mortar prepared at a higher W:C ratio. Figures 6 and 7 depict the loss of ammonia as a function of time for mortars prepared using Rockport and Bowen fly ash, respectively. Initially, within approximately 24 hrs of the beginning of the experiment, the loss rate was relatively high for both mortars. However, the low W:C ratio mortar exhibited a decrease in the loss rate earlier than the higher W:C ratio material. The result was a greater loss of ammonia in the latter. This is likely caused by a greater porosity and diffusivity in the higher W:C ratio mortar, since it is well known that an increase in the W:C ratio, and a decrease in cement content, causes increases in the coefficient of diffusion of concrete (e.g. Costa et al., 1992). Furthermore, the porosity is mainly controlled by the W:C ratio (Neville, 1996).

The mortar experiments also revealed that, unlike aqueous solutions, the rate of ammonia loss occurs in two “stages”: a rapid rate followed by a much slower, essentially linear rate that occurred after approximately 24 hours of curing and persisted throughout the remainder of the 3 week experiment. Furthermore, at the cessation of the experiment, greater than 80% of the ammonia was calculated to have remained within the mortar. These data indicate that ammonia could continue to evolve from the mortar for a long time after placement, although the rate would be very slow (approximately 0.5 mg/L of N per day). In fact, at the end of each experiment the mortar cylinders were capped and set aside. After two weeks the ammonia concentration in the 1 L head-space was measured in the Rockport mortar samples using detector tubes. The gas concentrations within the cylinders were 60 ppm and 85 ppm for the low W:C and high W:C mortars, respectively, thus confirming that ammonia continued to diffuse out of the mortar.

CONCLUSIONS

Based on the experimental results to-date, the following conclusions can be made that relate to ammonia loss from mortar:

1. Ammonia in fly ash exerts a negligible influence on the unconfined compressive strength of mortar.
2. The type of ammonium salt present on fly ash does not exert a significant effect on ammonia odors emanating from mortar or on the loss rate.
3. During the three-week experiments, ammonia release from mortar occurred at two rates: an initial rapid rate, followed by a much slower, nearly linear rate that persisted over the course of the three week-long experiments. Measurements taken several weeks after this indicated that ammonia continued to diffuse out of the mortars.
4. Under the conditions selected for the experiments (i.e. 1 L/min air flow, 20°C), greater than 80% of the initial ammonia concentration remained within the mortar at the end of three weeks.

5. Ammonia loss occurs at an overall faster rate from a high W:C mortar than from a low W:C mortar. The different rates probably result from the low W:C mix being less porous than the high W:C counterpart.

An important consideration regarding the data is that they pertain only to the experimental conditions employed, that is, 20°C with a flow rate of 1 L/min. Therefore, additional testing will be conducted at a different temperature, and at several different air flow rates. The latter will be completed to determine if the ammonia loss rate is limited by the concentration of the ammonia in the “head-space”, or by diffusion through the mortar. However, it is evident that a large proportion of ammonia remains in mortar after several weeks curing, and will continue to diffuse from the material for an extended period. Furthermore, the proportion of water added to the mix will significantly influence the concentration of ammonia within the hardened mortar. Therefore, several long-term experiments will need to be conducted to observe the diffusion rate of ammonia from different mortar mixes over the course of several months.

REFERENCES

American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE), *Ventilation for Acceptable Indoor Air Quality*, ANSI/ASHRAE 62-1999 - Published standard. (Supersedes ASHRAE Standard 62-1989).

Costa, U., Facchetti, M. and Massazza, F., Ninth International Congress on the Chemistry of Cement, Vol. 5, pp. 107-114, 1992.

Golden, D.M., Proceedings: 14th International Symposium on Management and Use of Coal Combustion Products (CCPs), Vol. 1, pp. 4-1 to 4-19, EPRI, Palo Alto, CA: 2001.1001158, 2001.

Jordan, T.D. and Casper, M.A., 1995 Joint Power Generation Conference, Vol. 4, ASME 1995, PWR-Vol. 29, pp. 147-151.

Labconco Corporation, *A Guide to Kjeldahl Nitrogen Determination: Methods and Apparatus*, www.labconco.com/pdf/kjeldahl/index.shtml, 1998.

Majors, R.K. and Rathbone, R.F., Proceedings: 14th International Symposium on Management and Use of Coal Combustion Products (CCPs), Vol. 1, pp. 8-1 to 8-8, EPRI, Palo Alto, CA: 2001.1001158, 2001.

National Institute for Occupational Safety and Health (NIOSH), *Ammonia: Method 6015 Issue 2*, 1994.

National Institute for Occupational Safety and Health (NIOSH), *Ammonia by IC, Method 6016 Issue 1*, 1996.

Neville, A.M., *Properties of Concrete*, 4th Edition, 844 pp., Wiley and Sons, New York.

Occupational Safety and Health Administration (OSHA) Technical Center, *Ammonia in Workplace Atmospheres - Solid Sorbent* (by R.G. Adler), OSHA-SLTC Method No. ID-188, Revised 1991.

Occupational Safety and Health Administration (OSHA) Technical Center, *OSHA Analytical Methods Manual*, OSHA-SLCAL Method No. ID-164, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1985.

Richards, F.A., *The Determination of Ammonia in Aqueous Solution*, Technical Report No. 84-3, Fisheries Bioassay Laboratory, Montana State University, Bozeman, Montana, 1984.

Table 1. Source and General Information for Fly Ash Samples

Sample	Company (State)	Ammonia Injection	Coal Type
Bowen	Southern Co. (GA)	None	Central App. Bit.
Mill Creek	LG&E (KY)	None	Northern App. Bit.
Rockport	AEP (IN)	None	App. Bit./Subbit. blend
Conesville	AEP (OH)	ESP Conditioning	Northern App. Bit.
Belews Creek	Duke Power (NC)	ESP Conditioning	Central App. Bit.
Yates Unit 5	Southern Co. (GA)	ESP Conditioning	Central App. Bit.

* App. Bit. = Appalachian, Bituminous rank, Subbit. = Subbituminous rank

Table 2. ASTM C 618 Data for Fly Ash Samples

Sample	Moisture (%, as-recvd)	LOI (%, dry)	SO₃ (%, dry)	Si+Al+Fe (%, oxides)	+325 Mesh (%, dry)
Bowen	0.1	2.1	0.3	89.4	19.9
Mill Creek	0.1	1.7	0.8	88.1	21.4
Rockport	0.1	0.9	0.7	70.3	20.4
Conesville	0.1	1.2	0.4	89.3	19.5
Belews Creek	0.1	4.3	<0.1	92.9	33.9
Yates (Unit 5)	0.1	8.1	0.1	92.0	29.0

Table 3. Chemical Composition of Fly Ash Samples

Sample	C (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	Ammonia (mg N/kg ash)
Bowen	1.5	54.5	28.3	6.6	2.4	1.2	0.4	2.5	1.1	0
Mill Crk	1.5	49.5	20.7	17.8	4.3	1.0	0.5	2.8	1.1	0
Rockpt	0.7	42.3	22.7	5.3	16.0	4.0	1.4	1.2	1.4	0
Consvl	0.7	45.8	24.3	19.2	2.4	0.8	0.4	1.9	1.3	230
Belews	4.0	55.2	31.9	5.8	0.8	0.8	0.4	2.1	1.9	74
Yates	6.8	53.7	27.0	11.3	1.9	1.3	0.5	3.1	1.4	245

Table 4. Aggregate Testing Data

Aggregate Type	Moisture (%)	Sp.Grav. (SSD) ¹	Absorption (%)	Unit Wt. (kg/m ³)	Top Size (mm)	Fineness Modulus
Fine	4.4	2.63	1.54	na	4.75	2.77
Coarse	0.1	2.71	0.43	1561	19	na

¹SSD = saturated, surface dry condition

Table 5. Mortar Mix Proportions

Property/Component	UCS Mix	Low W:C Mix	High W:C Mix
Cement (g/L)	543	429	392
Fly Ash (g/L)	124	107	98
Sand (g/L)	1,226	1,475	1,349
Water (g/L)	314	260	324
W:C+P	0.471	0.485	0.661
Yield (L) ¹	1.002	1.000	1.000

¹Assumes component specific gravities: cement = 3.15, fly ash = 2.40, sand = 2.64, water = 1.00

Table 6. Test of Ammonia Trapping Experimental Set-Up

Solution	pH	Starting Ammonia (mg/L as N)	Ending Ammonia (mg/L as N)
Source	10	200	10
Trap #1	4.7	<0.1	191
Trap #2	4.5	<0.1	<0.1

Table 7. Unconfined Compressive Strength of Mortar

Sample	7-Day UCS (PSI)	7-Day % of Control	28-Day UCS (PSI)	28-Day % of Control
OPC Only	4330	100	5700	100
Bowen	4140	96	5560	98
Mill Creek	4400	102	6040	106
Rockport	4670	108	5810	102
Conesville	4070	94	5630	99
Belews Creek	4270	99	6120	107
Yates	3900	90	5450	96

Table 8. Unconfined Compressive Strength of Mortar with Added Ammonia

Fly Ash Used In Mortar	Ammonia Concentration (fly ash basis)					
	0 mg/kg Ammonia		100 mg/kg Ammonia		200 mg/kg Ammonia	
	7-Day	28-Day	7-Day	28-Day	7-Day	28-Day
Bowen	4140	5560	4580	5550	4230	5610
Mill Creek	4400	6040	4370	5700	4760	5300
Rockport	4670	5810	4630	5820	4720	5730



Figure 1. Laboratory mixer used to prepare mortar.

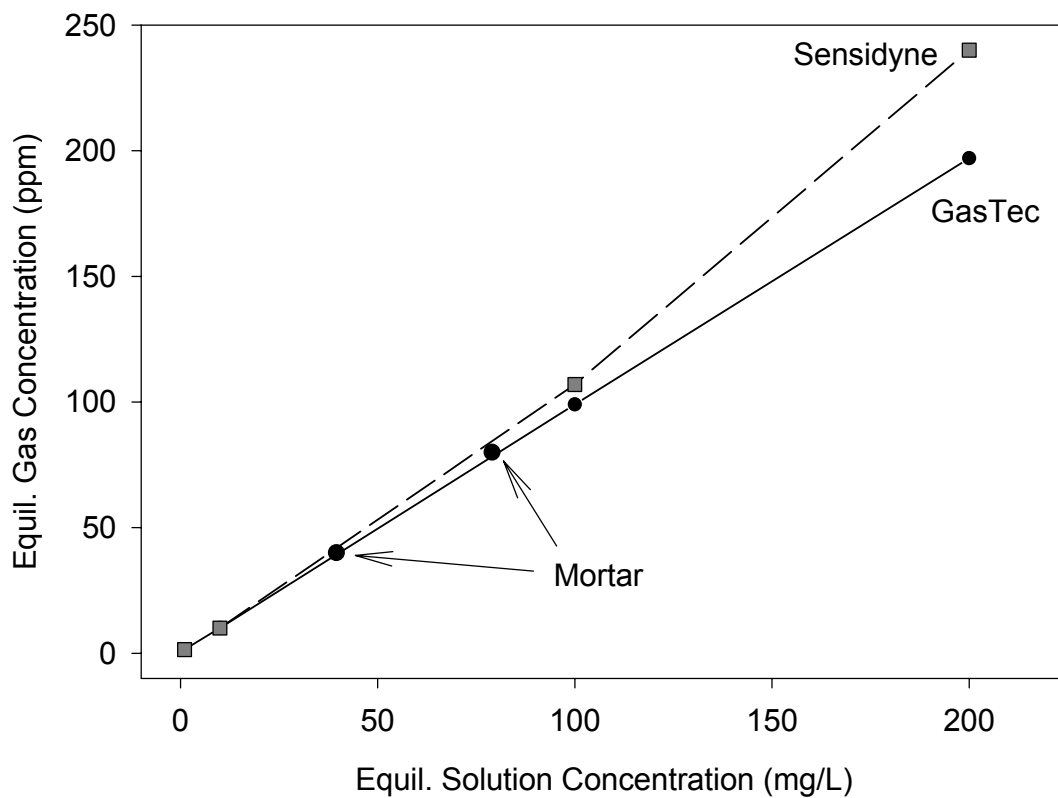


Figure 2. Equilibrium gaseous ammonia measurements using Sensidyne and GasTec detection tubes.

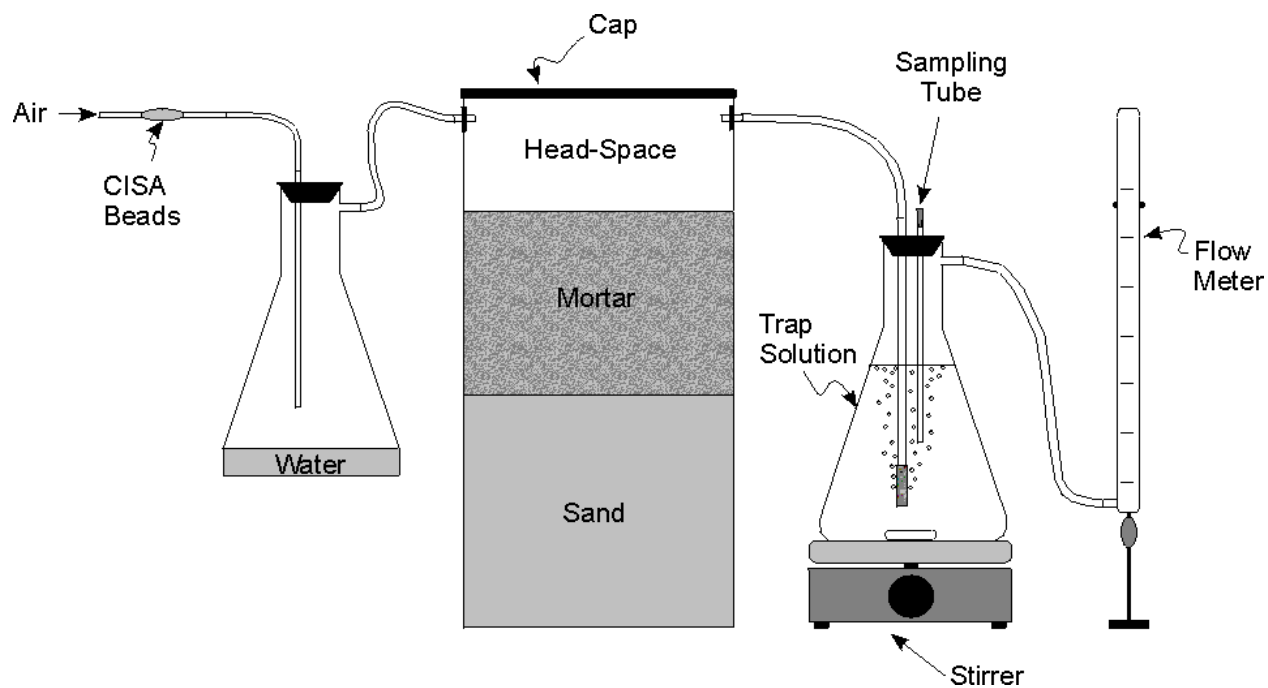


Figure 3. Experimental apparatus used for the measurement of the rate of ammonia loss from mortar.

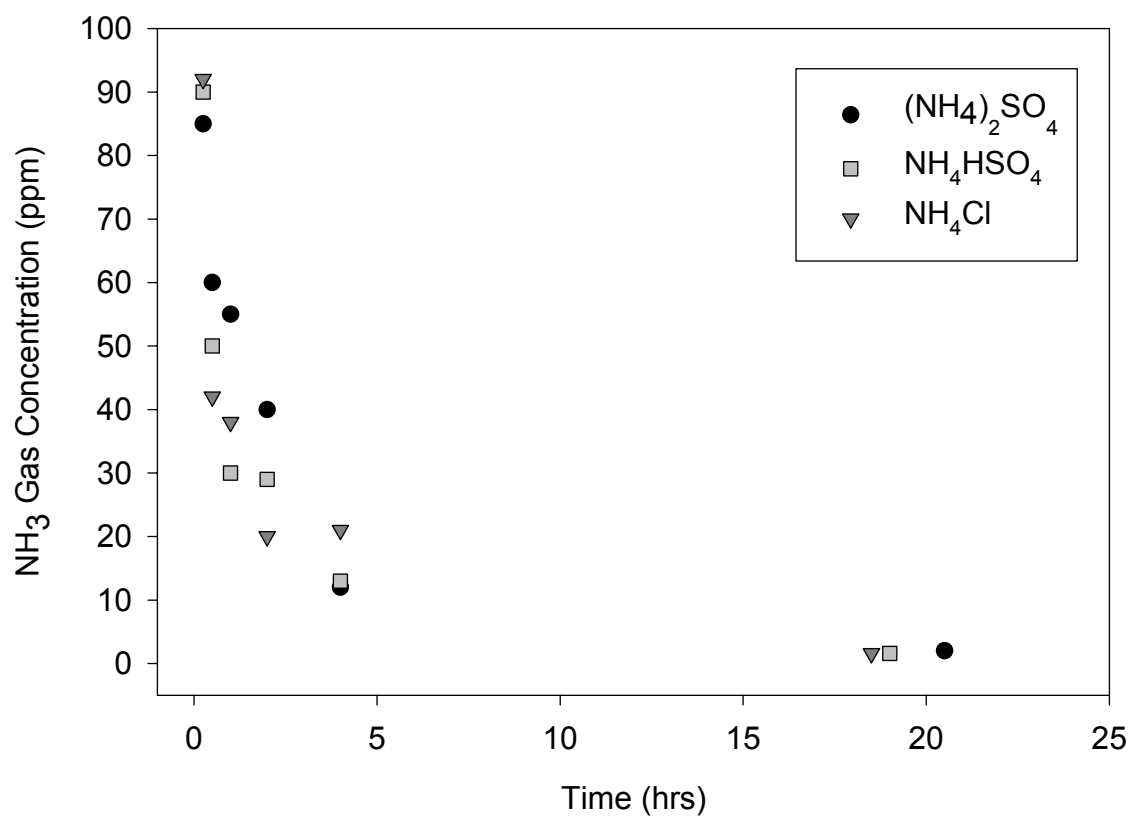


Figure 4. The effect of ammonium salt type on ammonia loss from mortar.

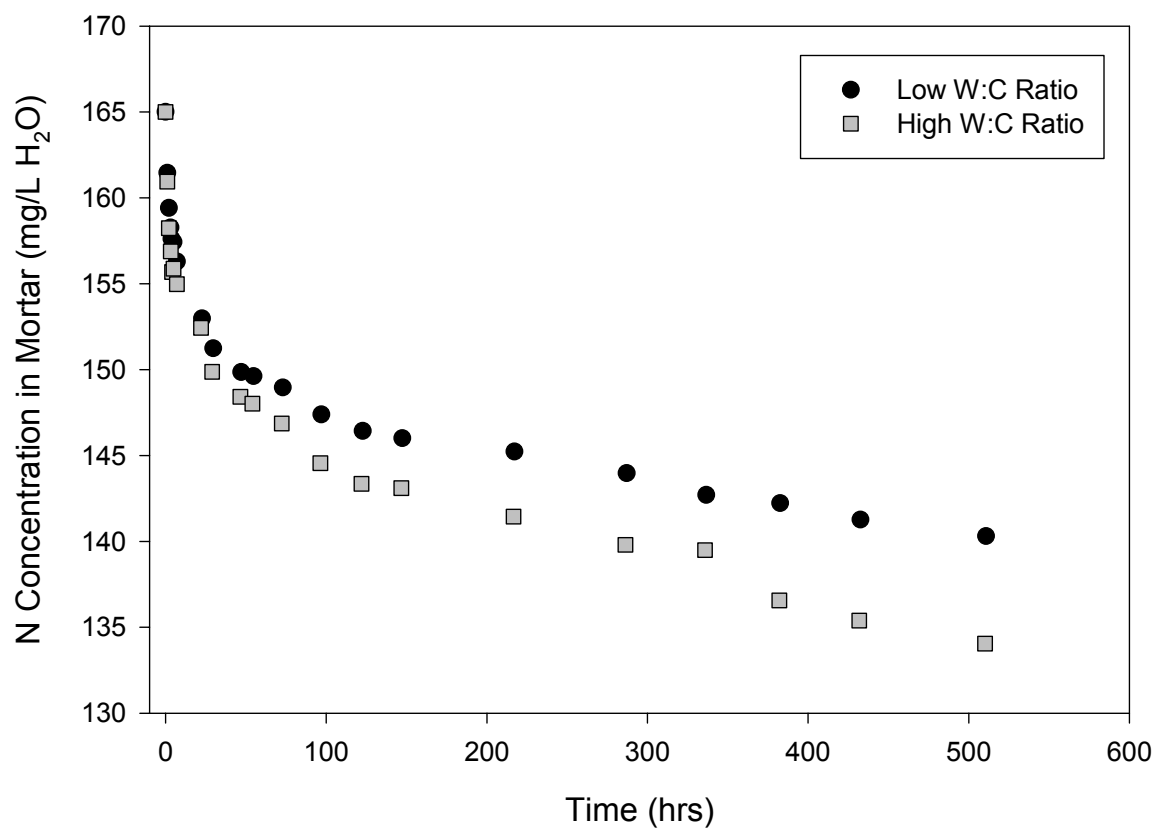


Figure 5. Effect of W:C ratio on ammonia loss from mortar: Rockport fly ash.

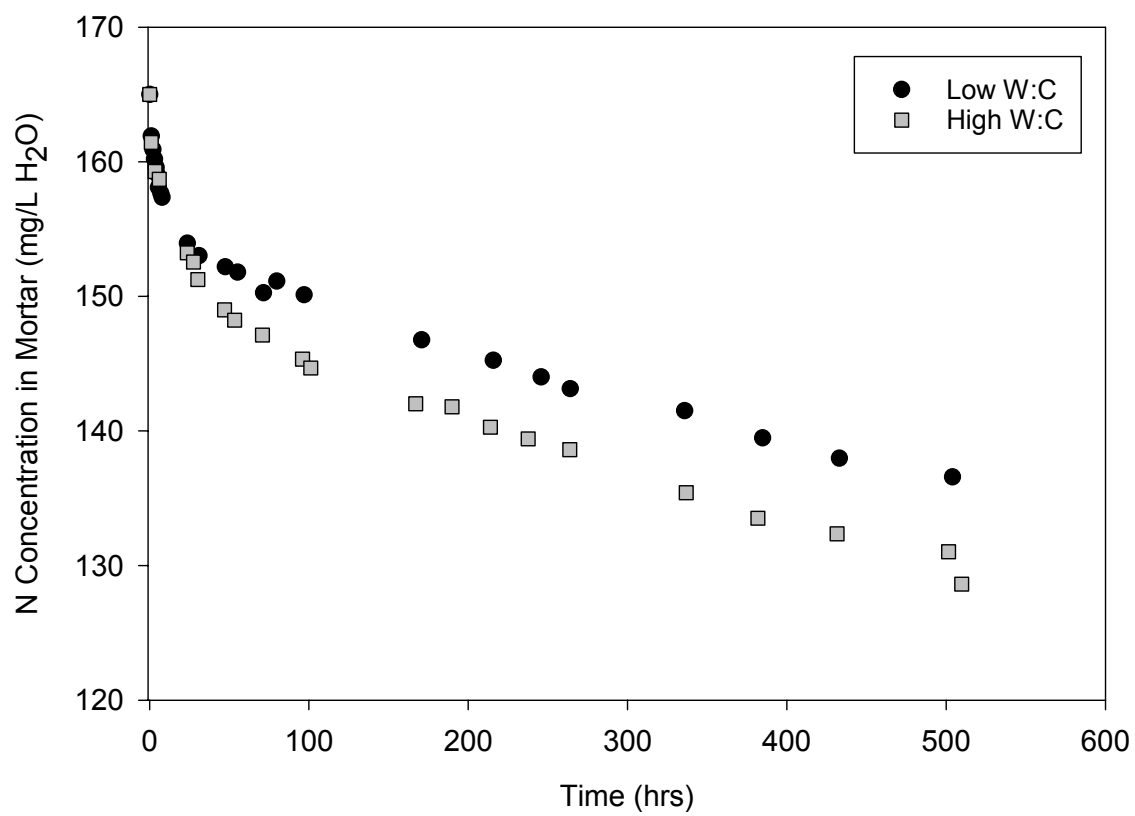


Figure 6. Effect of W:C ratio on ammonia loss from mortar: Bowen fly ash.