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Rates of Ammonia Loss from Mortar

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KEYWORDS: ammonia, fly ash, mortar, concrete

ABSTRACT

The presence of ammonia in fly ash, resulting from the injection of ammonia to control NO_x emissions, could create a major barrier to the utilization of fly ash in concrete. Practical guidelines on acceptable concentrations of ammonia in ash for specified applications, as well as for its safe handling are needed. The goal of this work is to develop a better understanding of the behavior of ammonia-laden ash in Portland cement-based products. The technical approach entails the measurement of ammonia release from mortar, concrete, and controlled low-strength material (i.e. flowable fill). This paper presents results from controlled laboratory experiments designed to measure the evolution of ammonia from mortar.

INTRODUCTION

The reduction of NO_x emissions from coal-fired boilers will necessitate the use of ammonia injection in many systems, resulting in the deposition of ammonia on the fly ash. The presence of ammonia could create a major barrier to ash utilization in Portland cement products. Currently, fly ash addition to these products as a pozzolanic admixture accounts for its single largest use[1]. There is a real potential for significant odor problems to exist during placement and finishing of concrete. Long-term emission of ammonia from the concrete is also a potential problem. Current research at the University of Kentucky CAER, in conjunction with Boral Material Technologies (BMTI), LaFarge, ISG Resources, and Southern Company, is being conducted with the objective of developing sound, practical guidelines for use of ammoniated fly ash. This paper presents the results of a portion of the work, specifically, from experiments designed to measure the rate of ammonia loss from mortar. The purpose of working with mortar was to begin with a less complicated material before acquiring data on a more complex concrete system.

EXPERIMENTAL

Fly Ash Sampling

Samples of fly ash were obtained from the ESP hoppers at six utilities, three of which currently inject ammonia into the flue gas (these samples are referred to herein as ammoniated ash). The fly ash samples were stored in tightly sealed 55 gallon drums.

Chemical and Physical Analysis of Fly Ash

Each fly ash sampled was characterized to determine if it met ASTM specifications for use as a concrete admixture (ASTM C 618). The data indicated that all of the fly ashes conformed to ASTM specifications with the exception of the "Y" fly ash, which contained excessive carbon. The ammonia content of the ammoniated fly ash samples was measured by mixing 50 g of fly ash with 150 ml de-ionized water in a polyethylene bottle. The mixtures were shaken periodically for approximately 48 hours, whereupon the solution was filtered. The filtrate pH was adjusted to 11-12, and the ammonia content measured using an Orion 95-12 NH_3 electrode. The quantity of ammonia present in the ash was then calculated on an ammonia-as-nitrogen basis (Table 1.)

Mortar Preparation
Mortar batches were prepared in accordance with ASTM C 305, using ordinary Portland cement, fly ash, de-ionized water and standard sand. Two mixes were designed to represent a range of water:cement (cement + fly ash) ratios, and both utilized a 20% replacement of cement with fly ash. The low W:C mix was an ASTM C 109 "standard mortar" (W:C = 0.485), whereas the high W:C Mix had a W:C ratio = 0.661 and a much higher flow. Ammonia was added to mortars prepared with non-ammoniated fly ash by dissolving ammonium sulfate in the water at a specific concentration. No additional ammonia was added to mortar containing ammoniated fly ash. To minimize ammonia loss during the mortar mixing the space between the mixing bowl top and the mixer head was enclosed and sealed using a flexible plastic sheet.

Unconfined Compressive Strength (UCS) of Mortar
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. UCS data were acquired after 7 days and 28 days.

Ammonia Loss from Mortar
<u>Ammonia Loss Rate</u>
The experimental set-up devised for these experiments is shown in Figure 1. A measured flow of air was passed through a sealed 15 cm diameter X 30.5 cm long (6 in. X 12 in.) plastic cylinder that contained a layer of mortar. Ammonia was removed from the incoming air using carbon impregnated with sulfuric acid (CISA) beads, followed by humidification through a flask containing water. The effluent from the mortar cylinder was diffused through a 250 ml Erlenmeyer flask containing a magnesium acetate-acetic acid trap solution. The trap solution was periodically sampled and the ammonium ion concentration measured using an Orion ammonium electrode. Evaporation of the trap solution was compensated for by adding fresh solution each day in sufficient quantity to return the flask to it's initial weight.

The selection of air flow rate was based on the requirement for the ventilation of a residential living area (ASHRAE 62-1999)[2], which is 450 L/min-person. For example, a basement room size of 70 m^2 with 5 persons would require ventilation of 2250 L/min/70 m^2, which equals 32.1 L/min-m^2. Our laboratory experimental design represents a cylindrical segment of the room with a surface area of 0.018 m^2. It follows that the air flow for the cylinder is 0.58 L/min, which would represent a living space ventilated to minimum standards. However, a smaller basement or additional persons would require a greater ventilation rate. Therefore, air flow rates between 0.5 and 4.0 L/min were chosen for our mortar experiments to represent a range of ventilation conditions.

Accumulation of Ammonia in an Enclosed Space Over Fresh Mortar

One of the major concerns regarding the use of ammoniated fly ash in mortar and concrete is the potential exposure of workers to high levels of ammonia. In this context, a key issue is the maximum concentration of ammonia allowable in fly ash, below which worker safety would not be jeopardized. Therefore, an experimental procedure was designed to address this issue. An 11 cm thick layer of ammonia-laden mortar was placed into a vertical 15.2 cm (6 in.) i.d. diameter section of PVC pipe that was capped on the bottom. A 213 cm (7 ft) tall section of identical pipe (capped at the top) was then placed over the bottom section and sealed to it using a rubber-lined pipe clamp. Holes were drilled at several locations (10, 40, and 70 in. above the mortar) along the length of the upper pipe section to allow measurement of ammonia concentration inside the pipe (between measurements the holes were plugged). Two of these holes were sometimes used as an inlet and outlet for air flow through the pipe. Ammonia concentration was measured using GasTec ammonia detection tubes.

RESULTS AND DISCUSSION

Unconfined Compressive Strength (UCS)

Table 2 presents the results of the UCS testing for mortar prepared using the different fly ash samples. It is evident that the presence of ammonia has no discernible effect on strength. This result is not unexpected since it has been previously reported that ammonia has no negative impact on concrete strength[3].

Ammonia Loss from Mortar

Effect of Water:Cementitious Ratio

In these experiments, ammonia was added to the mix water at a concentration of 400 mg ammonia (as N) per kg of fly ash for the low W:C ratio mortar, and 545 mg/kg for the high W:C ratio mix. This was done to keep the solution concentration constant for both mixes. However, in practice when using ammoniated ash, the ammonia level will be higher for a low W:C mix than for a high W:C mix because the higher proportion of water in the latter dilutes the ammonia solution concentration. The air flow was 1 L/min.

The results indicated that the overall ammonia loss rate was greater for the mortar prepared at a higher W:C ratio. An example of the data is provided in Figure 2. Initially, within approximately 24 hrs, the loss rate was relatively high for both mortars. However, the low W:C mortar exhibited a decrease in the rate sooner than the higher W:C material. The result was a greater loss of ammonia in the latter. This is possibly caused by a greater amount of bleed water coming to the surface of the high W:C mortar. Furthermore, the high W:C mortar will have a greater porosity and thus diffusivity: it is well known that an increase in the W:C ratio, and a decrease in cement content, causes increases in the porosity and coefficient of diffusion of concrete[4,5]. At the cessation of the experiment, greater than 80% of the ammonia remained within the mortars. These data indicate that ammonia could continue to evolve from the mortar for a prolonged period after placement, although the rate would be very slow.

Effect of Ventilation Rate

According to work by Weiler[6] the rate of ammonia loss from water to the atmosphere is a function of pH, temperature, the area:volume ratio of the water body, and the wind speed. Thus, for mortar (pH > 12) at constant temperature and thickness the ammonia loss rate should be limited by the air ventilation rate over the mortar. Figure 3 depicts the effect of ventilation rate on ammonia loss from low W:C mortars containing 400 mg N/kg fly ash. The data indicate that an increase in ventilation does indeed increase the ammonia loss rate from mortar. Compared with a 1 L/min air flow, ventilation of the cylinder with 4 L/min of fresh air for three weeks causes a loss of 25% of the total ammonia compared with only 15% for the former. These data indicate that a well-ventilated space could substantially increase the loss of ammonia from mortar and, by inference, a concrete slab.

Effect of Fly Ash Type

The rates of ammonia loss from mortars prepared using different fly ashes are presented in Figures 4 and 5. For the low-calcium Class F fly ashes, the source of the ash has a negligible influence on the loss rate. However, mortar prepared using the higher-calcium (16% CaO) “Rpt” fly ash evolved ammonia at a slightly slower rate than the Class F ash mortars (Figure 4). This is possibly related to the faster rate of strength development that occurs when high-calcium fly ash is used in mortar and concrete than when Class F fly ash is used.

Accumulation of Ammonia in an Enclosed Space Over Fresh Mortar

Table 3 provides the measured concentrations of ammonia at different heights above a mortar prepared with an ammonia concentration equivalent to 100 mg N/kg “Bn” ash, with no ventilation in the pipe. During the first 2 hours of measurement the ammonia concentration was highest near the mortar surface. However, after 2 hours the ammonia concentration was homogeneous from top to bottom. This trend was observed for all of the experiments without ventilation. The maximum concentration was 17 ppm which is below the 25 ppm TWA and 35 ppm PEL limits recommended by NIOSH[7]. Increasing the ammonia concentration to 200 mg/kg (non-ammoniated ash) and 245 mg/kg (ammoniated ash) resulted in air concentrations as high as 35 ppm and 38 ppm, respectively (Table 4), which exceed NIOSH limits. A flow of 0.5 L/min air (representing a low degree of residential ventilation) lowered the maximum ammonia-in-air concentration for the 200 mg N/kg ash mortar to 20 ppm. These data suggest that, under the conditions employed for the experiments (i.e. 0.485 W:C ratio, 20% cement replacement with fly ash, 20^{o}C) the maximum concentration of fly ash ammonia for confined-space applications is 100 mg N/kg, whereas for other applications with at least a modicum of ventilation the maximum concentration is approximately 200 mg/kg.

The effect of mortar flow is shown in Table 5, which provides the results of two experiments where the flow was increased by using a W:C ratio of 0.661 (“Bn” fly ash) and by adding 667 ml of a mid-range water reducing admixture per 100 kg of cement + fly ash (10 oz/100 lbs) for the “Y U5" mix. It is evident that increasing the flow of the mortar mix can substantially increase ammonia evolution from the material into the air, even though the high W:C “Bn” mortar contains a lower ammonia concentration in the water than the low W:C mortar (from dilution). This effect seems to be associated with an increase in the quantity of bleed water that occurs at the surface of the mortar, which would effectively bring ammonia with it. Furthermore, excessive bleed can introduce channels in the mortar which could provide an additional conduit for ammonia release.

CONCLUSIONS

1. Ammonia has a negligible effect on compressive strength of mortar.
2. Mortar containing a high calcium fly ash loses ammonia at a slightly slower rate than mortar prepared using low-calcium fly ash.
3. The source of Class F ash has no effect on ammonia loss from mortar.
4. A higher water:cementitious material (W:C) ratio causes ammonia to be lost from mortar at an overall higher rate than a low W:C ratio: this difference occurs primarily in the first 24 hours.
5. In a confined space application, mortar data (@ 20% cement replacement with fly ash) suggest that the fly ash ammonia concentration should not exceed 100 mg N/kg ash. For most other applications, the maximum concentration is approximately 200 mg/kg.
6. Depending on the W:C ratio and the air ventilation rate, between 70-85% of ammonia remains in a mortar slab after 3 weeks, at which the loss rate has slowed dramatically.

Additional work is required to determine if the data acquired using mortars is applicable to concrete. Consequently the study of ammonia loss from concrete is currently being investigated as a part of this project.

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ACKNOWLEDGMENTS

This project is supported by the U.S. Department of Energy NETL, through cooperative agreement DE-FC26-00NT40908, with additional support provided by Boral Material Technologies Inc., ISG Resources Inc., LaFarge North America, and Southern Company Services.

Table 1. Chemical Composition of Fly Ash Samples

Sample	C (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	LOI (%)	NH_3 (mg/kg)
Bn	1.5	54.5	28.3	6.6	2.4	1.2	0.4	2.1	0
MC	1.5	49.5	20.7	17.8	4.3	1.0	0.5	1.7	0
Rpt	0.7	42.3	22.7	5.3	16.0	4.0	1.4	0.9	0
Cnv	0.7	45.8	24.3	19.2	2.4	0.8	0.4	1.2	230
BC	4.0	55.2	31.9	5.8	0.8	0.8	0.4	4.3	74
Y (U5)	6.8	53.7	27.0	11.3	1.9	1.3	0.5	8.1	245

Table 2. 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
Bn	4140	5560	4580	5550	4230	5610
MC	4400	6040	4370	5700	4760	5300
Rpt	4670	5810	4630	5820	4720	5730

Table 3. Ammonia in Air Above Fresh Mortar:
100 mg N/kg ash, no ventilation

Time (hrs)	Ammonia Concentration in the Air (ppm)		
	Bottom	Middle	Top
0	0	0	0
0.5	11	10	7
1	16	14	12
2	16	16	16
6	17	17	17
22	12	12	13
52	9	9	9

Table 4. Maximum Ammonia Level in Air Above Fresh Mortar: Varying Ammonia Concentration with no Air Flow

	Ammonia Concentration in Ash (mg/kg)			
	74[1]	**100**	**200**	**245[1]**
Concentration (ppm)	11	17	35	38

[1]Ammoniated fly ash samples used in the mortar mix

Table 5. Maximum Ammonia Level in Air Above Fresh Mortar

Fly Ash Sample	Low Flow Mortar	High Flow Mortar
Bn (100 mg N/kg ash)[1]	17 ppm	20 ppm
Y U5 (245 mg N/kg ash)[2]	38 ppm	55 ppm

[1]Low flow = low W:C ratio mix, high flow = high W:C ratio mix
[2]Low flow = low W:C ratio mix, high flow = low W:C ratio mix with plasticizer

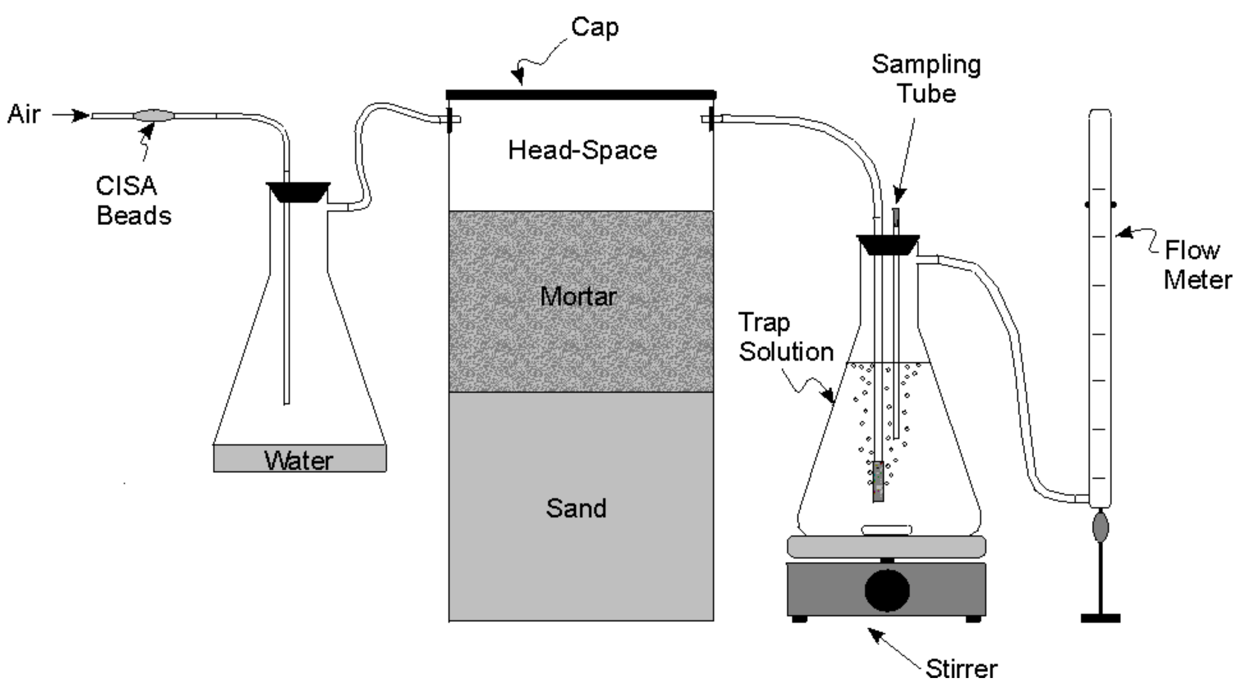

Figure 1. Schematic diagram of apparatus to measure ammonia loss from mortar.

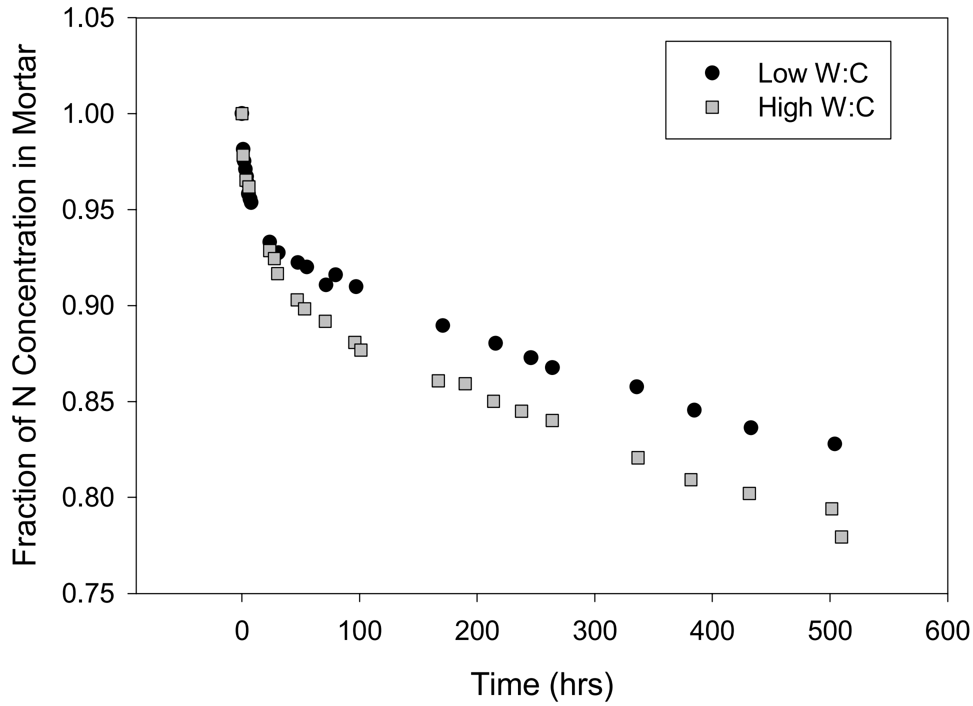

Figure 2. Ammonia loss from mortar prepared with “Bn” ash. Fraction of N refers to starting concentration in the mortar.

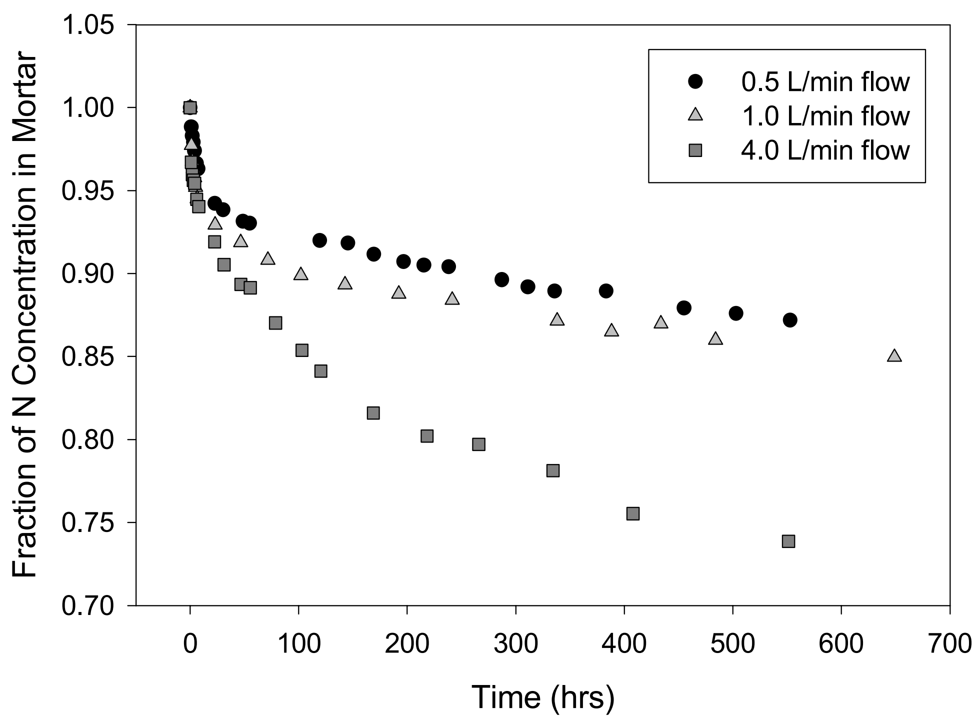

Figure 3. Ammonia loss from mortar at several different ventilation rates (“Bn” ash).

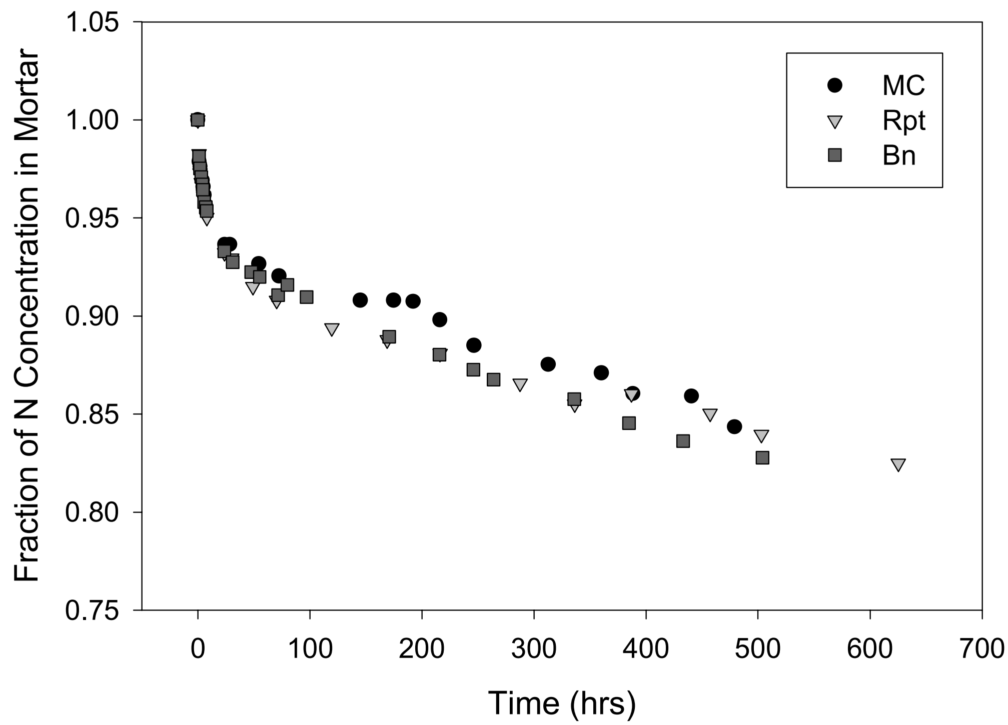

Figure 4. Ammonia loss from mortar prepared using different non-ammoniated ashes.

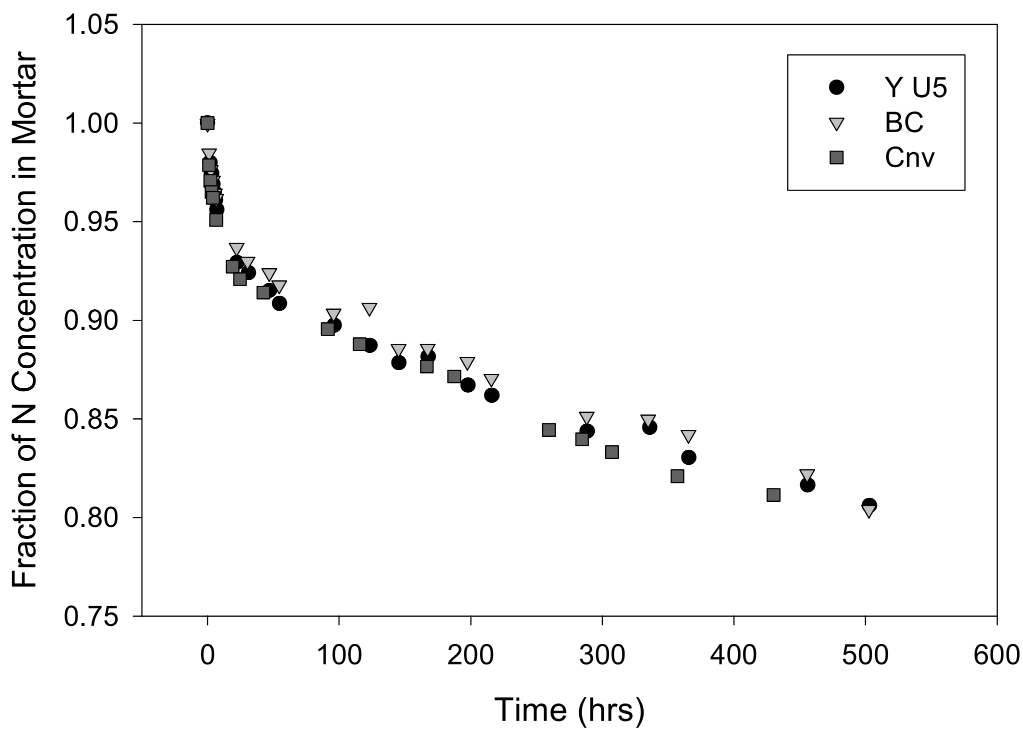

Figure 5. Ammonia loss from mortar prepared using different ammoniated ashes.