

Techniques for Measuring Ammonia In Fly Ash, Mortar, and Concrete

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ABSTRACT

The presence of ammonia in fly ash, that is being used in mortar and concrete, is an increasing concern in the U.S. mainly due to the installation SCR systems. When the SCR catalyst is new, contamination of the fly ash with ammonia is generally not a concern. However, as the catalyst in the SCR ages and becomes less efficient, the ammonia slip increases and results in a greater amount of ammonium salt being precipitated on the fly ash. The increase in ammonia concentration is compounded by variability that can occur on a day-to-day basis. When marketing ammonia-laden fly ash for use in mortar and concrete it is imperative that the concentration of ammonia is known. However, there currently is no widely accepted or "standard" method for ammonia measurement in fly ash. This paper describes two methods that have been developed and used by the University of Kentucky CAER and Boral Materials Technologies, Inc. One of the methods uses gas detection tubes and can provide an accurate determination within five to ten minutes. Thus it is suitable as a rapid field technique. The other method employs a gas-sensing electrode and requires a longer period of time to complete the measurement. However, the latter method can also be used to determine the quantity of ammonia in fresh mortar and concrete

INTRODUCTION

The Clean Air Act Amendments of 1990 have inadvertently presented one of the most significant barriers to the high-volume use of coal combustion fly ash in concrete, mortar, and flowable fills, through the required reductions in NO_x emissions at coal-fired electric utility boilers. Combustion modification using low NO_x burners can achieve NO_x reductions of up to 50%, and typically result in substantial increases in fly ash carbon content. Selective catalytic reduction (SCR) and non-catalytic reduction (SNCR) will be necessary additions to many coal-fired electric generating utilities to meet emissions requirements. Unfortunately, these post-combustion ammonia-injection processes result in ammonia contamination of the fly ash.

The use of ammoniated fly ash in Portland cement-based projects creates a host of potential odor issues. As a part of the overall problem, one barrier that is

emerging is the paucity of information available regarding behavior of the ammonia in concrete and flowable fills, acceptable levels of ammonia in the fly ash, and appropriate analytical techniques to measure the ammonia concentration. In fact, the analytical technique used to measure the ammonia content of a fly ash is often not clearly known by the plant personnel who use the data. The lack of a routine standard measurement method can generate a degree of uncertainty regarding the quality of ammoniated fly ash when it is used in cementitious materials. A rapid and inexpensive technique for measuring ammonia in fly ash could be used at a power plant to frequently monitor ammonia concentrations. Fly ash containing high levels of ammonia can be identified before it is incorporated into a cementitious system. This would help ensure that the fly ash being utilized is of a more consistent and acceptable quality. This paper presents several analytical methods that have been useful for measuring the ammonia concentration in fly ash, mortar, and concrete.

Established Ammonia Measurement Techniques

There are currently no standard methods for the measurement of ammonia content in fly ash, mortar, or concrete. A standard method needs to be robust, inexpensive, rapid, and simple to be useful in the "field". There are many techniques available for the determination of ammonia in water and the air, although many are somewhat tedious and involve a substantial amount of glassware, chemicals, and preparation steps. A summary of methods is provided below.

Colorimetric Techniques (Water)

1. Nesslerization: ASTM D 1426; **EPA 350.2**
2. Indophenol
 - i. Phenol, NaDTT, Na-nitroferricyanide: **EPA 349.0**
 - ii. Phenol, hypochlorite, Na-nitroprusside: **EPA 350.1**
 - iii. Na-salicylate, hypochlorite, Na-nitroferricyanide: **USGS I-2525**

Titration (Water)

1. Distillation into excess H_2SO_4 soln; back titration with NaOH
2. Distillation into H_3BO_3 soln; titration with H_2SO_4 : **EPA 350.2**

Ion Chromatography (Water)

Potentiometry (Water)

- NH_3 Gas-Sensing electrode
- pH raised to convert all ammonia to NH_3
 - **ASTM 1426; EPA 350.3**

Acid Trapping (Air)

1. H_2SO_4 trap, measure NH_3 with electrode: **OSHA ID-164**
2. H_3BO_3 trap, measure NH_3 by titration with H_2SO_4

Detector Tubes (Air)

1. Diffusion tubes
2. CISA (carbon impregnated with sulfuric acid) tubes: **OSHA ID-188;**
NIOSH 6016

The techniques presented herein ostensibly are modifications of two of these techniques: diffusion tube sampling of ammonia in air, and potentiometry.

Boral Material Technologies Inc. Ammonia Field Test

Scientists at Boral developed a “field test” for the determination of ammonia on fly ash in response to a utility incorporating ammonia in the conditioning of flue gases to increase ESP efficiency. Other methods used for the determination of ammonia that were evaluated are the Kjeldahl method for nitrogen determination and an ammonia ion selective electrode (ISE). Although the Kjeldahl determination and the ISE proved to be an accurate and reliable method for determining the ammonia content of a fly ash sample, it was determined that a more robust test was needed for utilization in the field by plant personnel. In cooperation with the University of Kentucky CAER and Chemron Incorporated, Boral developed a test based on the conversion of the ammonium ion to ammonia under basic pH conditions. The concentration of ammonia is then determined using gas detector tubes. This value is then used to calculate the amount of ammonia in the fly ash based on correlative studies using the Kjeldahl determination of nitrogen.

The procedure summary is as follows:

1. Place 4.45 grams of fly ash into a clean 500 ml Erlenmeyer flask
2. Add 92 ml of tap water into the flask. Gently swirl the flask until all of the ash is wet.
3. Add 10 grams of NaOH (sodium hydroxide) pellets into the flask and place the vented stopper on top, gently pressing the stopper until well seated.
4. With your thumb over the vent holes, gently swirl the flask until the sodium hydroxide pellets have dissolved.
5. Break off ends of Gastec detector tube and place into the syringe with the arrow pointing towards the syringe.
6. Place the tube into the vent hole in the stopper. Pull one complete stroke. Wait for the white indicator to show on the end of the plunger. Remove the tube from the stopper and read the ppm from the scale.
7. If the ammonia concentration is greater than 100ppm, repeat the test but only pull ½ stroke. Multiply ppm results by 2.

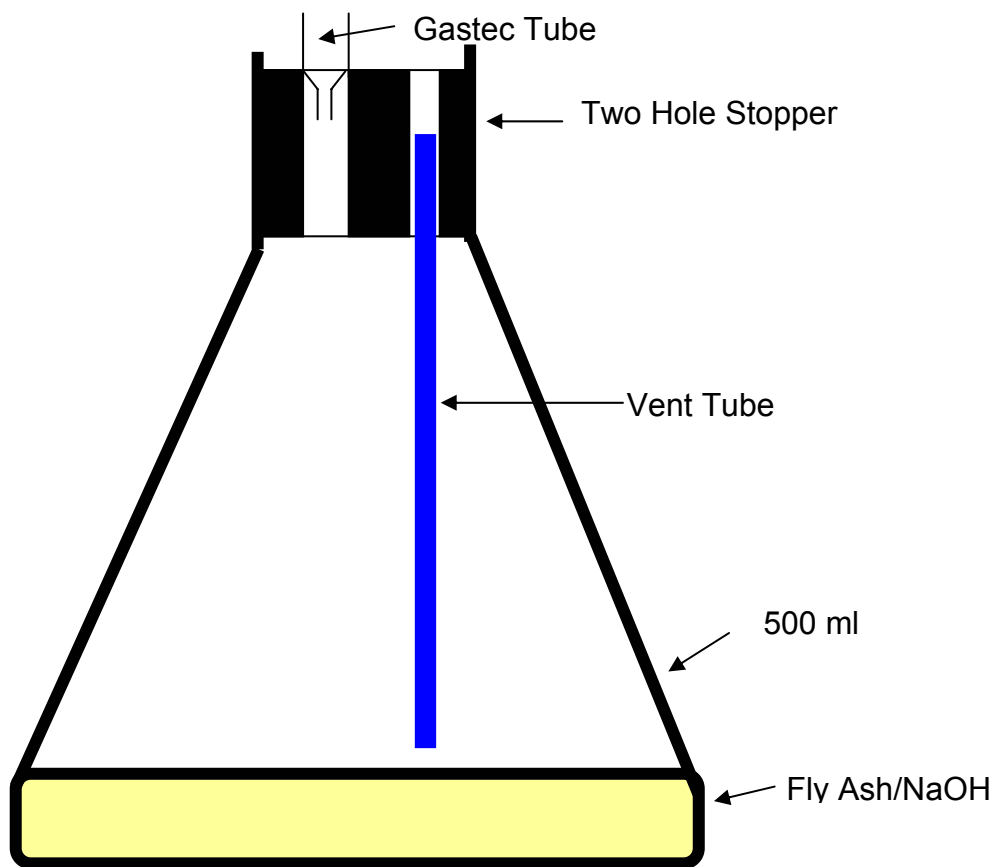
The sodium hydroxide pellets cause a significant increase in temperature. This temperature increase can cause variability in the test results. Therefore, the test duration needs to be carefully controlled at 3 minutes. A stopwatch is used to time the experiment, which begins at the moment the NaOH pellets are added to the water.

Prior to beginning the test, the Erlenmeyer flask must be calibrated. Fill a clean 500 ml Erlenmeyer flask with water. Gently press a two-hole stopper into the

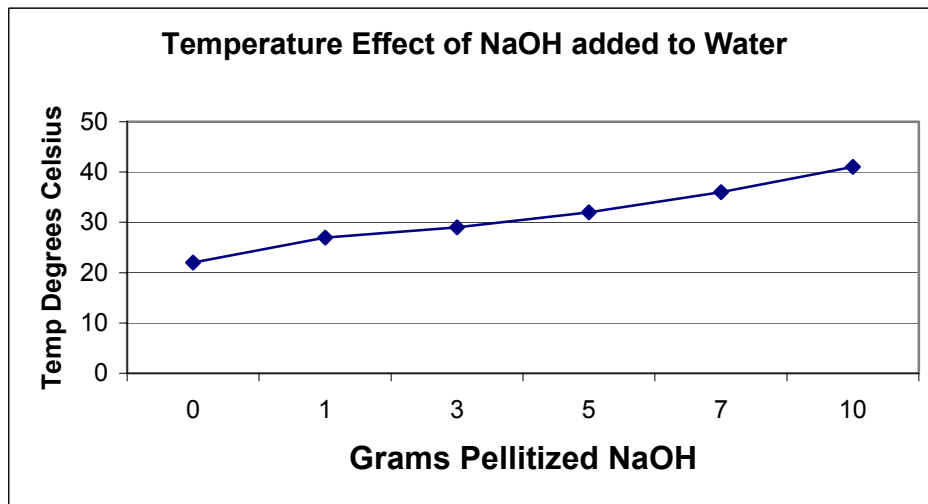
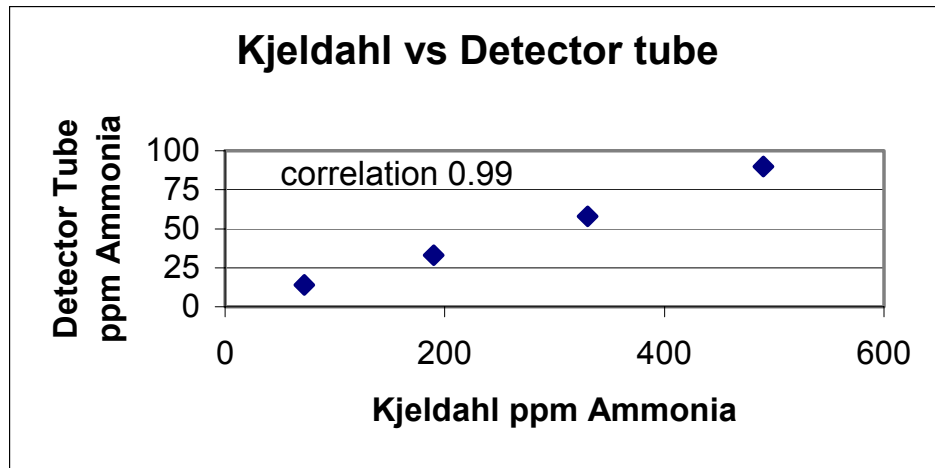
flask until well seated. Wipe any excess water from the top of the stopper. Carefully remove the stopper as not to spill any of the water. Pour the water from the erlenmeyer flask into a graduated cylinder. Record the total volume of water.

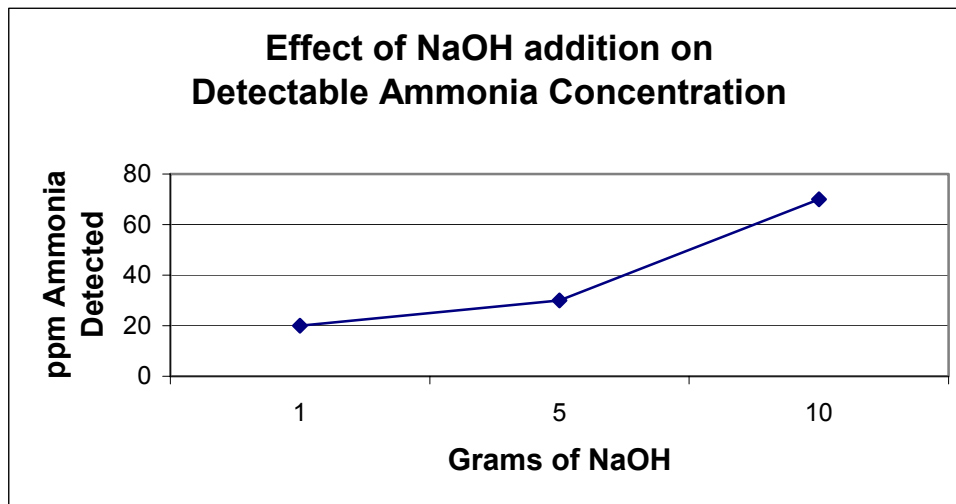
To determine the fly ash sample size, subtract 100 from the total volume of the erlenmeyer flask determined in the previous paragraph and divide this number by 100. Use the result as the weight in grams of fly ash to use in the test. For example, if the total volume of Erlenmeyer flask is 545ml, it follows that $545 - 100 = 445$ and $445 / 100 = 4.45$ g of fly ash.

An illustration of the test apparatus is provided below:



A good correlation exists between the field test and the Kjeldahl determination of Nitrogen. One variable that significantly impacts the results of the field test is temperature. For this reason, field personnel are required to have on hand a supply of potable tap water that is maintained at “room temperature” or 22 to 25 degrees Celsius. The test was also founded on the utilization of 10 grams of pelletized sodium hydroxide instead of a prepared caustic stock solution or flake material. The 10 grams not only shifts the pH but also provides heat to the sample to increase the amount of ammonia driven out of the sample solution and into the headspace of the testing apparatus.





The Boral Field Ammonia Test was developed to provide a robust field test that allowed limited operator maintenance and influence. It is used extensively in the field by BMTI, however, it is only used in the BMTI laboratory to correlate with ISE and Kjeldahl test results to confirm field test performance. A variable that can significantly influence the test results is temperature, however, having utilized the test for a significant period of time, it is felt that this variable can be controlled to the extent that reliable information can be gained.

Potentiometry Method

This method utilizes an ammonia gas-sensing electrode to determine the ammonia concentration in an aqueous solution. We have found that the electrode can be used for determination of ammonia in fly ash, mortar, and concrete because it is fairly robust, easy to use, and provides accurate, repeatable results. A significant benefit is that it is not significantly affected by solution turbidity.

Procedure Summary for Fly Ash

Prepare one liter of a 0.1M aqueous solution of NaOH. Mix 50 g of fly ash with 150 ml of the 0.1M NaOH solution in a 250 ml plastic bottle. Shake the bottle either on a shaker table or occasionally by hand for 10 minutes and let stand for at least 5 minutes. Calibrate the electrode as per the manufacturers instructions using 10 and 100 mg/L standards. Decant the supernatant into a plastic beaker or small bottle, and determine NH_3 concentration of the supernatant using the electrode. The ammonia content of the fly ash (in mg/kg) = the solution concentration (mg/L) x 3. The rationale for selecting such a high proportion of fly ash is two-fold: for most ammoniated fly ashes (i.e. 30 to 300 mg NH_3 /kg ash) the solution concentration will be between 10 and 100 mg/L, and the multiplication factor of 3 to obtain ash ammonia concentration will minimize multiplying the analytical error. However, a smaller proportion of fly ash could be

used. Furthermore, NaOH is not necessary for ammonia determination in Class C fly ash or Portland cement because of the inherently high pH.

Tables 1 and 2 provide a summary of the effects of several experimental factors that were tested: filtering versus decanting, and fly ash soak time. From these data it was concluded that filtering results in a slightly lower concentration, possibly caused by ammonia loss from solution during the filtering procedure. The data also indicated that 15 minutes is a sufficient soak time. Data for various fly ash samples and a cement sample to which known concentrations of ammonium sulfate have been added are provided in Table 3.

Table 1. Filtering vs. Decanting

Solution Preparation Method	Solution Concentration (mg/L)	Ash Concentration (mg/kg)
Decanting	68	204
Filtering	66	198

Table 2. Effect of Soak Time on Measured NH₃ Concentration

Ash Soak Time (min)	Solution Concentration (mg/L)	Ash Concentration (mg/kg)
5	57	171
17	57	171
30	56	168
45	56	168
60	56	168
75	56	168

Table 3. Results for Fly Ash and Portland Cement

Ash or Cement Sample	NH₃ Actual (mg/kg)	NH₃ Measured (mg/kg)
Mo	150	149
Co	188	186
Ro	150	149
MC- low	59	55
MC- high	296	277
Bo	152	151
Ch	150	149
Cement	150	149

Procedure for Mortar and Concrete

The technique for measuring ammonia concentration in mortar and concrete uses an ammonia-sensing gas electrode to determine the ammonia concentration of an air headspace above the material. This technique is based on the equilibrium of ammonia and water vapor concentration in the concrete paste with that in the headspace. The fresh mortar or concrete is placed into a polyethylene bottle that has a solid cap containing a 1.9 cm hole fitted with a rubber grommet and temporarily plugged with a foam stopper. The material is agitated for 5 minutes, whereupon the ammonia electrode is inserted into the grommated hole so that the end of the electrode is above the concrete/mortar surface (Figure 2). The ammonia concentration of the water in the concrete/mortar is then obtained by comparing the voltage readout with those from standards. Knowledge of the mix proportions allows for the calculation of the fly ash ammonia content.

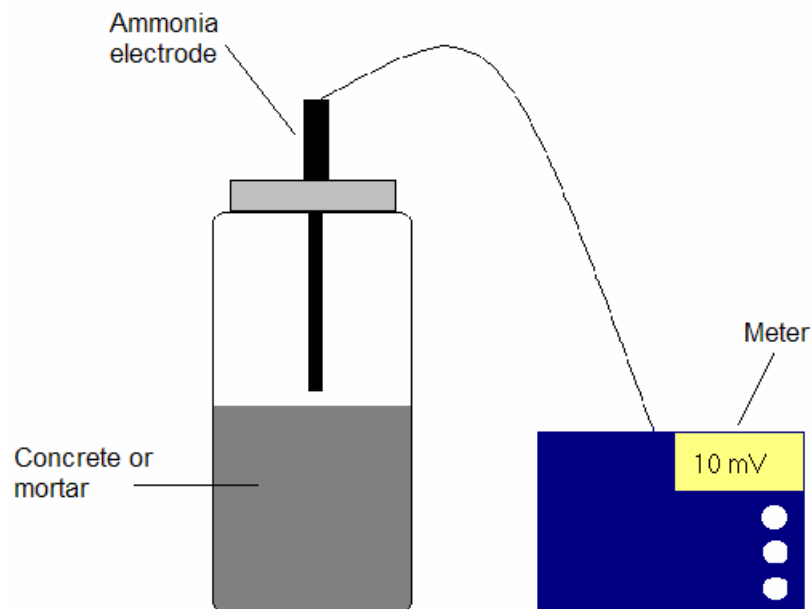


Figure 2. Apparatus for measuring ammonia concentration of concrete and mortar.

This technique has been checked for accuracy by using cement paste, mortar, and concrete with known concentrations of ammonia. The results of these tests are provided in Table 4, and indicate that the technique provided an accurate measure of ammonia in the concrete and mortar, although it gave slightly elevated concentrations for the cement paste. The procedure has since been used successfully in practice many times. The only significant problem that has been encountered is for low-slump concrete. In this case, the measured concentrations have been too low, probably caused by equilibrium not being established between the ammonia in the concrete and that in the headspace. For these materials, a known quantity of water can be added to the concrete to

raise the slump prior to measurement of the ammonia concentration, as long as the operator accounts for the additional water (i.e. dilution) in the subsequent calculations.

Table 4. Ammonia Concentration of Fresh Paste, Mortar, and Concrete

Material	Actual NH₃ (mg/L H₂O)	Measured NH₃ (mg/L H₂O)
Paste ¹	122	134
Mortar ²	122	120
Concrete ³	122	120

¹Cement, ash, water; ²Cement, ash, sand, water; ³Cement, ash, sand, gravel, water

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