Testing the Ammonia Content of Class F Fly Ash

Steven Roy Butler[1]
[1]Lafarge North America, Lockport, Illinois, USA

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ABSTRACT

A method to test for ammonia in fly ash was developed using Gastec detector tubes that provided results that were proportional to the ASTM C311-08 Ion Selective Electrode method. The Lafarge method detects ammonia in the enclosed space over stirred slurry of fly ash and sodium hydroxide solution. Results with Class F were not as uniformly proportional as results with this method and Class C samples. This paper will explore further modifications to the sodium hydroxide solution to improve the proportionality of the results.   This paper contains:

Results using the Lafarge method on Class F samples with 10, 15, 20 and 25% solutions of sodium hydroxide.

Repetitive testing using the same solution by multiple technicians.

Measure of the pH of the fly ash slurry to quantify the differences in the sodium hydroxide solution.

An expression that correlates the results by the Lafarge method and the results on the same samples by the ASTM C311-07 Ion Selective Electrode.

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EXECUTIVE SUMMARY

The testing of ammonia in two sources of fly ash presented a useful method for quantifying ammonia in Class C sources. The same five Class F samples were tested by the same method but with different testing solutions. The Lafarge Ammonia Reading (LAR) result, at 1% concentration sodium hydroxide testing solution and 20⁰ C, was closer to the ISE ammonia value. The LAR result, at 10% concentration sodium hydroxide testing solution and 20⁰ C, was a more accurate approximation of the ISE ammonia value. The pH of the 1% sodium hydroxide was tested to ensure the solution was sufficiently alkaline to dissociate the ammonium sulfate in the fly ash. The five samples were tested repeatedly with 1% concentration of sodium hydroxide at 20⁰ C and 10% concentration at 50⁰ C. At an elevated temperature the LAR varied with small changes in temperature. The 1% testing solution at 20⁰ C was the better compromise of proximity and best correlation to the ISE ammonia results.

SIGNIFICANT RESEARCH

The origin reference to our work on this subject was the excellent paper by Rathbone and Majors [1] that has appeared in several different forms in the literature. We consider their approach to this subject essential for understanding ammonia on fly ash for marketers of coal combustion products. The apparatus we used came directly from their work. The work by Guo [2] on the reaction of sulfur dioxide with ammonia explains the different reaction products that are actually formed under different gas conditions as a model of the air pre-heater. Bai [3, 4] studied particle formation of ammonia sulfate reactions at ambient and slightly elevated temperatures and trace water conditions. Keener [5] took the particle formation of Bai and went farther into the effect of having fly ash particles in the same space as the water vapor, sulfate, and ammonia. Keener found the amount of water vapor present had a significant effect on the size of the ammonium sulfate particles. These papers formed the basis for our theory on the sources of variability and the proportionality of our ammonia readings to the testing solution.

BACKGROUND

Lafarge developed a method for testing the ammonia content of fly ash using Gastec detector tubes and has submitted a paper to ASTM for peer review. "Testing ammonia in two sources of fly ash" describes the method in depth as to the steps and precautions to take in testing fly ash for ammonia with Gastec tubes. Essentially the method uses the Gastec tubes to quantify the ammonia in the air over slurried fly ash and sodium hydroxide testing solution; that is stirred vigorously for five minutes at 50⁰

C in a closed flask before being analyzed. The method is referred to as the Lafarge Ammonia Reading – LAR. The paper presents the results of the method on five Class C and five Class F samples analyzed by the method approved by ASTM C 311-08 [6] (ASTM D 1426 [7] Ion Selective Electrode - ISE). The ISE results were compared to the results of testing the same samples by the EPA 350.1 [8] (colorimetric analysis of Indophenol Blue – IBC). A simple linear regression was made to correlate the IBC method to the ISE method approved by ASTM. The R^2 of the IBC to the ISE for Class C was 0.96 and 0.85 for the Class F. The objective of the Lafarge method development in this paper was to meet or to improve on the R^2 correlation of the EPA method to the ASTM method.

The previous paper presents results of the LAR with 10% sodium hydroxide testing solution on the five Class C samples and an average R^2 correlation was 0.92. In testing of Class F fly ash with the same 10% sodium hydroxide testing solution the average R^2 was 0.69 because the two technicians found very different results from their splits of the same samples.

The earlier paper also analyzed two of the Class C and two Class F fly ash samples in a variety of solution concentrations of sodium hydroxide up to 10% to find a low intercept. The low intercept would mean the correlation to the ASTM method would work down to a very low equivalent concentration. Four samples of Class C and Class F with high and low ISE ammonia concentrations were tested with the LAR using a range of sodium hydroxide concentrations from a low of .625% up to 10%. The results with the higher sodium hydroxide testing solution for both classes measured more ammonia than the ISE detected on the same samples.

INTRODUCTION

The objective for this second paper on our development work was to identify a concentration of sodium hydroxide solution that achieved the better correlation to the ASTM D 1426 ISE method than the IBC method for both classes of fly ash.

We separated the objective into two parts that would make the Lafarge Ammonia Reading more acceptable for Class F fly ash. If the slope of the trendline of the graph of the ISE, as a function of the Lafarge Ammonia Reading (LAR) approached one, the LAR number would be essentially equivalent to the ISE result. This was called the proximity objective. If the R^2 of the trendline of the graph of the ISE, as a function of the LAR ammonia was higher than the R^2 correlation of the graph of the ISE to the EPA method (IBC), then the conversion from the LAR could be made with confidence. This will be called the accuracy objective. The linear regression expression for the trendline is the equation to convert the

ammonia by the LAR to the ammonia by the ISE.

SAMPLES AND METHOD SUMMARY

The same five Class F samples tested for the previous paper were used in this work. The ammonia was measured in duplicate by TEI analytical [9] using the D 1426 ISE method. Their results follow in figure 1.
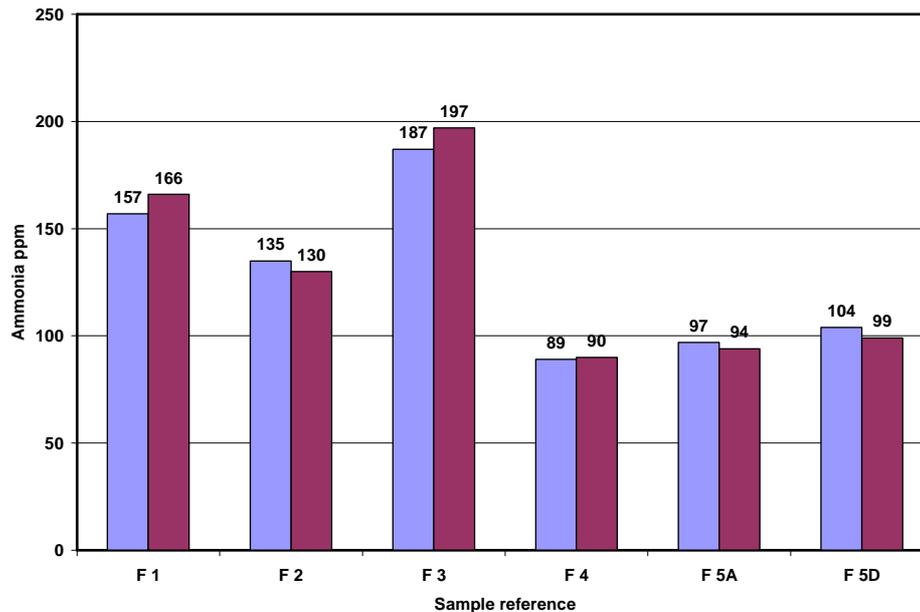

Figure 1 Ammonia of Class F samples by Ion Selective Electrode.

The repeats of the ISE results on the same sample can vary from each other by as much as 10 ppm or as little as 1. This is despite a significant effort to homogenize the samples before and during testing as described in the first paper. We ran ISE repeats of two splits (F5) of the same sample to examine the variability in different ways. The variability between splits of the same sample appeared to be consistent with the repeats of the same split sample.

The testing apparatus is the Boral experimental apparatus and the same as described in the first paper. The apparatus is shown in Figure 2.
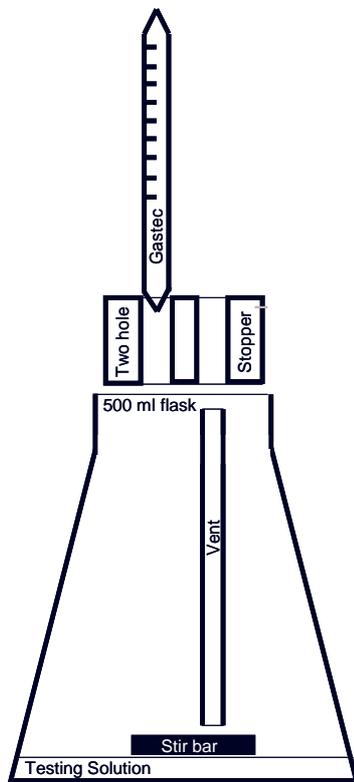
Figure 2 Experimental setup after Boral.

The 500 ml Erlenmeyer flask was selected for the large opening that allows for the fly ash sample to be charged quickly. The number 10 two-hole stopper allows for both the vent tube and the Gastec detector tube to be mounted in place without difficulty. The stopper opening above the vent tube is covered with adhesive tape during the stirring process and between Gastec measurements. This tape is peeled back when the pump (not shown) aspirates the gas from inside the flask and then is immediately replaced.

The testing logic of the LAR is adapted from the Gastec manual for the 3L and 3La ammonia detector tubes used in this study. For an unknown sample the first test is with 7.5 grams of sample and 70 ml of sodium hydroxide testing solution. The solution is heated and stirred to 50⁰ C in the flask. Then the fly ash sample is added and the flask is closed with the vent tube in one side of the stopper and the Gastec tube and the pump on the other side of the stopper as shown in figure 2. The vent tube is inserted in the stopper and closed with adhesive tape during the 5 minute stirring period on the hot plate to maintain the 50⁰ C temperature. The slurry is stirred at 500 rpm or until the slurry reaches the 150 ml mark on the beaker.

The first reading is taken with a 50 ml pull of the pump. If the initial reading on the tube is in the upper two thirds of the range, the reading is final and no further testing of that sample is required. If the initial reading is too high; restart with a smaller fly ash sample. As shown in figure 3, if the reading is too low; peel back the tape, pull 50 ml more gas from the flask, and replace the tape. Take the reading off the tube seeking a reading in the upper two thirds of the range of the tube. If the reading after 200 ml of gas sampling is still too low; double the quantity of fly ash in the testing solution and restart testing in a clean flask.
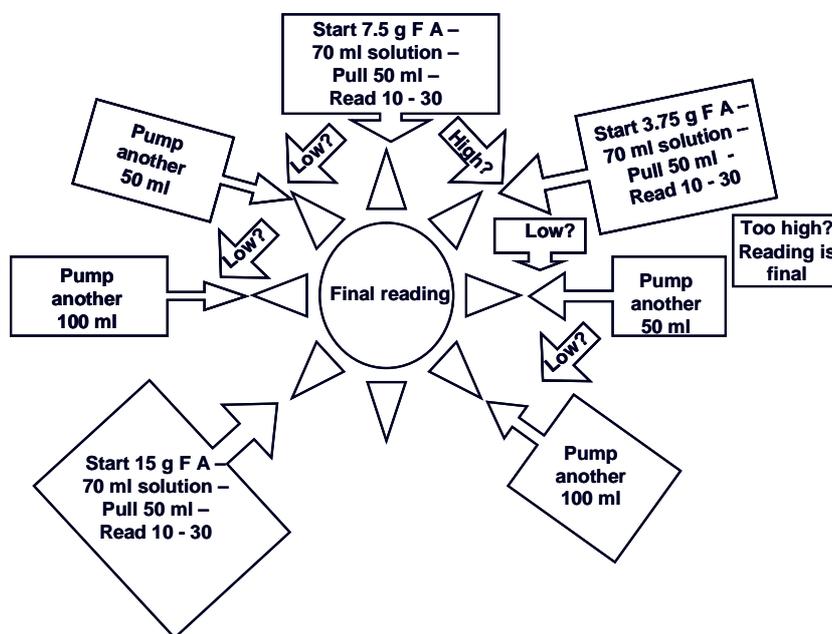

Figure 3 Lafarge ammonia testing protocol

In order to compare different fly ash additions and different volumes of gas used in the measure we use two correction factors. The correction for the dilution of the fly ash is the weight of the solution divided by the weight of the fly ash. For the starting point of 7.5 grams of fly ash in 70 grams of solution the dilution factor is 9.33. The correction factor for the Gastec tube comes from the calibration for each model of tube and is different for the several models of detector tubes. The 50 ml correction factor for the 3L tube is 2.6. If two 50 ml pulls are needed to get the reading on the tube to be in the 10 to 30 range for 3L tubes, the Gastec correction factor would be 1. The LAR is the reading on the tube, times the dilution factor, times the Gastec factor.

The metrics for progress toward the objectives in the study are the

Microsoft Excel trendline, or linear regression, expression; and the R² value of the scatter plot of the ISE ammonia result as a function of the Lafarge Ammonia result.

The search for a solution to the proximity objective was first priority. If the LAR value was close to the ISE value, it would be easy to compare fly ash tested by either the ISE or the LAR method. In the first paper we showed that the higher the sodium hydroxide concentration, the lower the slope of the linear regression expression, and the better the R² correlation for LAR to the ISE. We returned to low concentrations at 50⁰ and 20⁰ C to look for a higher slope value with an acceptable R² correlation.

RESULTS

In figure 4, the concentration of the sodium hydroxide is presented as percent solids of the testing solution. The results at 50⁰ C show the slope is slightly elevated at sodium hydroxide concentration near 1%; however the R² correlation is not improved and the values are three times higher. At concentrations over 1% the R² correlation actually decreased dramatically. The pH of the 1% testing solution with 15 grams of Class F fly ash was measured after 5 minutes of stirring at 50⁰ C and the result was 12.97. This result is well over the 11 pH where the ammonium sulfate is dissociated into ammonia.
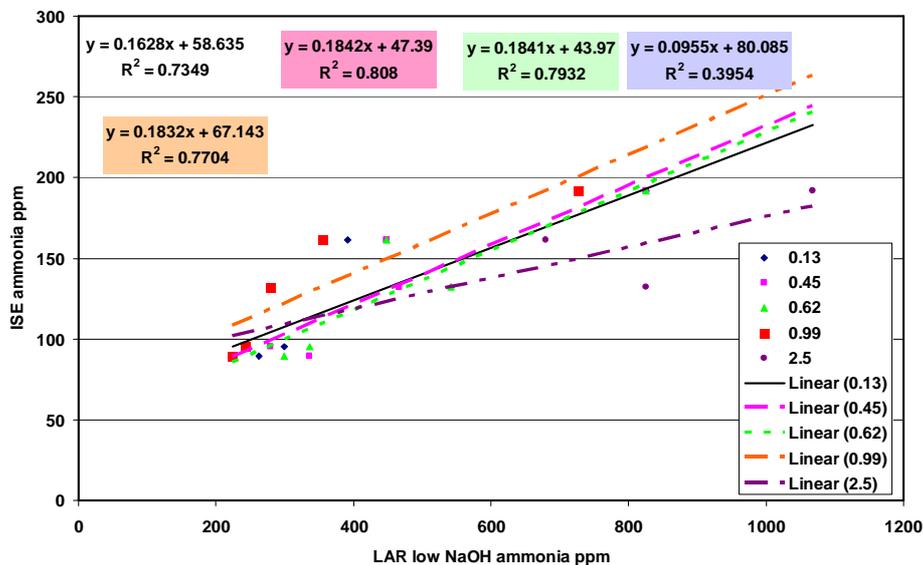

Figure 4 Correlation of ammonia by ISE to LAR at low sodium hydroxide concentrations at 50⁰ C.

The results in figure 5 are at low solution concentrations at 20º C. Here the slope is much higher, and the R² improve around 1% solids. The difficulty is that while the R² correlation improves at concentrations over 1%, the slope of the trendline goes down, and the LAR values move away from the ISE ammonia values. The pH of the 1% testing solution with 15 grams of Class F fly ash was measured after 5 minutes of stirring at 20º C and the result was 13.01.

Another observation of figure 4, and all the figures that follow, is the F1 result at 162 ppm by ISE is often far to the left of the trendline. This implies that the LAR trendline expression typically overestimates the ammonia of that sample, but only that one sample of the five. A hypothesis for that underestimation will be presented in the discussion.
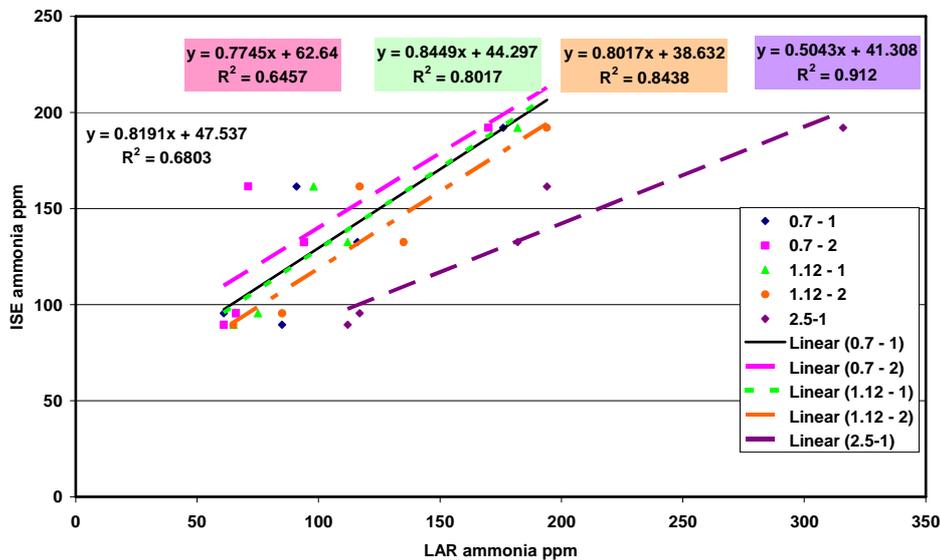

Figure 5 Correlation of ammonia by ISE to LAR at low sodium hydroxide concentrations and 20º C.

The proximity objective appears to be mostly achieved by modifying the Lafarge method to testing conditions at 20ºC with a 1% sodium hydroxide testing solution. The five Class F samples were tested in 10 repeats with the 1% testing solution at 20º C in order to establish an experimental error. Two technicians tested splits of the same five samples. The results of all the trials are presented in figure 6 to find the trendline expression and the R².
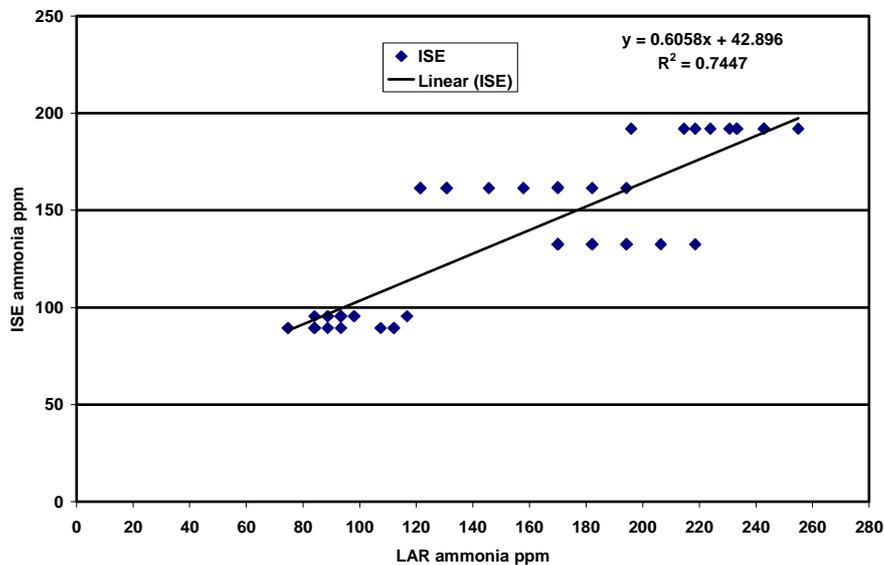
Figure 6 Correlation of ISE ammonia to LAR with 1% solution in 10 repeats.

The 1% testing solution performed well toward the proximity objective. Solving the linear regression expression for the benchmark ISE ammonia values of 100 ppm [10] for work in enclosed space and 150 ppm for concreting outside the LAR values would be 94 ppm and 177 ppm. The R² value is slightly lower than the target for the accuracy objective, but 0.74 is a very acceptable value. The RMSE for the results set is 20.1.

The previous work appeared to show a more accurate correlation at sodium Hydroxide concentrations over 10%. The pH of the 10% testing solution with 15 grams of Class F fly ash was measured after 5 minutes of stirring at 50⁰ C and result was 12.60. In this second study we present the results of testing solution at the 10% solution form the previous work and then 15%, 20%, and 25% sodium hydroxide at 50⁰ C. In figure 6 the progression of the linear regression equations from the first paper continues toward lower slope and higher R² correlation.
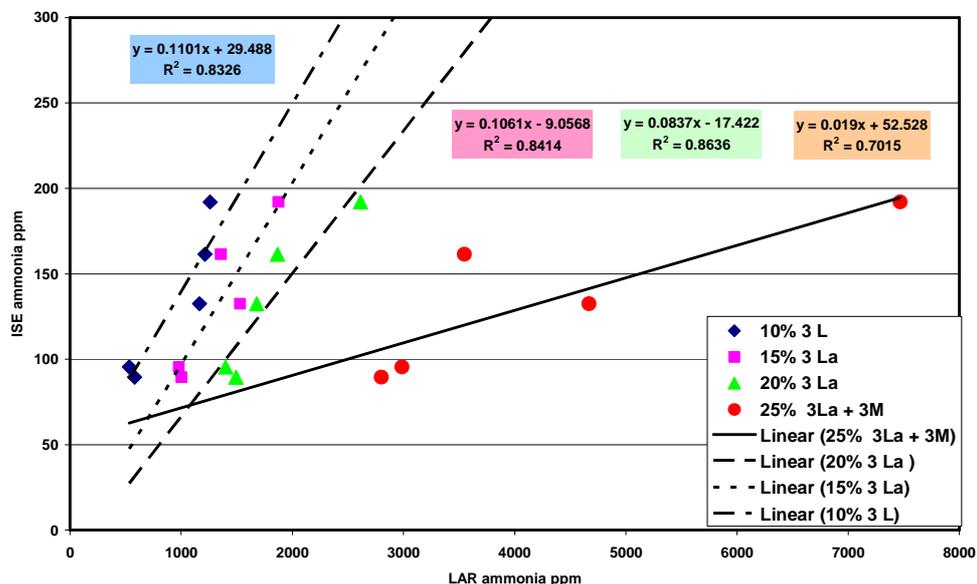
Figure 7 Correlation of ammonia by ISE to LAR at high sodium hydroxide concentrations at 50⁰ C.

In figure 7 we can see the correlation to the ISE continues with higher LAR at the higher sodium hydroxide concentrations up to 20%. At 25% sodium hydroxide the slope of the trendline changes markedly and the R^2 is lower. The extremely high ammonia readings suggested the ammonia reading might be elevated due to the presence of amines or hydrazine in the gases evolved from the testing slurry in the flask. The instructions from Gastec indicated that these compounds could interfere with the measure of ammonia using their detector tubes.

In order to resolve this question, 15 grams of Class F sample was reacted with the 25% sodium hydroxide solution and the gas analyzed by ICP-MS at TEI Analytical. The instrument did not find amine or hydrazine in the gas sample. The detection limit of the instrument may have been too high to measure amine or hydrazine from our small sample, but these compounds were not detected.

The falling R^2 at 25% was seen as an indication that high concentrated testing solution was not necessary. The question of tube accuracy over 10% sodium hydroxide testing solution was mostly resolved by the absence of amine and hydrazine. The hazards of handling high concentration sodium hydroxide solution at 50⁰ C made the selection of 10% sodium hydroxide solution an acceptable compromise for the repeat testing. The five Class F samples were tested repeatedly with the 10% testing solution at 50⁰ C in order to establish an experimental error. Two

technicians tested splits of the same 5 samples. The results of all the trials are combined in figure 9 to determine the trendline and R².
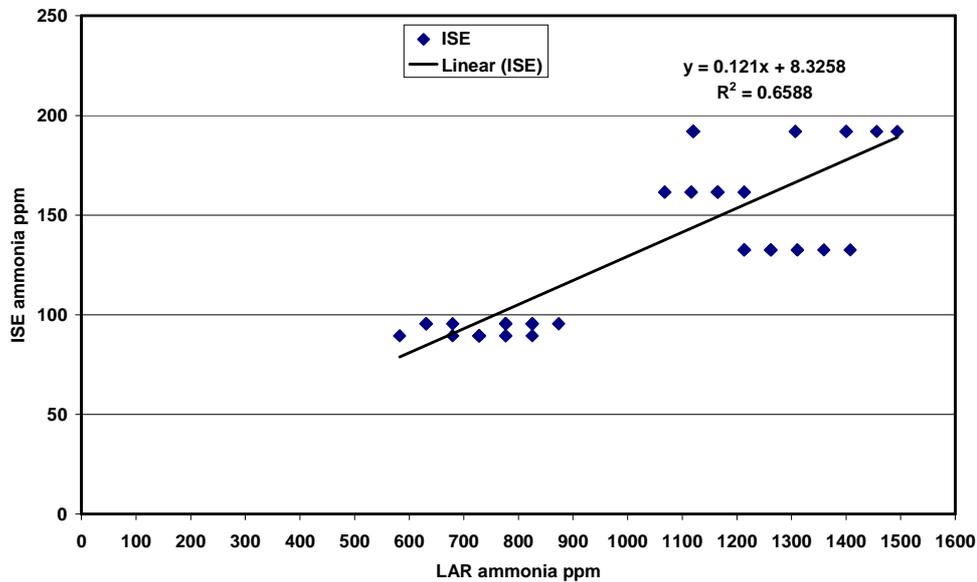

Figure 8 Correlation of ISE ammonia to LAR with 10% solution in 10 repeats.

The 10% testing solution did not perform well toward the accuracy objective. The R² value is lower than the value for the 10 repeats with 1% testing solution. Solving the linear regression expression for the benchmark ISE ammonia values of 100 ppm for work in enclosed space and 150 ppm for concreting outside the LAR values would be 757 ppm and 1170 ppm. These values would not be easy for the utility personnel or customers to interpret, and the R² value is slightly lower. The RMSE for the results set is 23.2. In addition the technicians found the temperature was critical to get comparable results.

DISCUSSION

The lower slope of the trendline expression is the result of higher LAR ammonia with increasing sodium hydroxide concentration in the testing solution. One hypothesis for the apparent proportionality is that the morphology of ammonium sulfate in the Class F is substantially different in the five different samples and is not fully dissolved in the testing solution of lower sodium hydroxide concentration. This is consistent with Bai's work on particle formation. Bai teaches that the ammonium sulfate particles change when the stoichiometry of the water vapor, ammonia and the sulfate change in the exhaust steam.   A different distribution of particle sizes would have a different specific surface area. If the testing

solution only dissolved the outer surface of these particles in a fixed time period; then the measurement result would be more dependent on the surface area than the mass of ammonium sulfate in the fly ash. Secondly, if the variation of the size of particles is large and the sample size is relatively small, then the potential for testing variation between samples and between repeats would be higher than if the particle size was small, uniform and the particles were uniformly distributed in the fly ash.

This hypothesis would interpret the ammonia reading in lower concentration testing solution as proportional to the specific surface area of the ammonium sulfate. The dilute testing solution would dissociate the ammonium off the surface of these particles. Then the reading by ISE, IBC, or the Lafarge method in lower solution concentration would not be an indication of the total ammonia in the fly ash. These readings would be a function of the specific surface of the ammonium sulfate and the kinetics of the dissolution into the testing solution. The higher concentration testing solution should have been immune to the surface area effect and at some point dissolved all the ammonium sulfate out of the fly ash. If there is no interference, the results at 25% show there is much more ammonium sulfate in the fly ash than was measured with a dilute testing solution.

In our efforts to achieve the objective of this work we raised the temperature, and used high speed stirring to dissolve more of the ammonium sulfate out of the fly ash sample. The temperature had significant effect on the LAR in the 10 repeats with two technicians. Our five minute mixing time should allow more ammonia to become dissolved into the testing solution and be diffused into the air in the flask where it can be measured by the Gastec detector tube. We increased the sodium hydroxide concentration until the R^2 peaked and the proportionality from raising the sodium hydroxide concentration disappeared at 25%.

Figures 6 and 8 show the trendline and the individual results grouped together at the level of the ISE result. These groups are always in the same position relative to the trendline. The lower groups are samples F4 and F5 and the trendline passes through the group. Sample F2 is at the 130 ISE level and sample F1 is at the 160 ISE level. Sample 3 is the high value at 192 ISE. The fact that three of the data groups do not fall on the trendline with either of the testing solutions and the groups have the same relative position to the trendline line is interesting.

If the trendline expression underestimated the correlation of the LAR to the ISE results, the group is the right of the trendline, and the particles of ammonium sulfate would be finer. This is to say finer than the other five samples in these tests. Finer particles generally have higher surface area. The LAR seemed to dissolve more ammonia and have higher ammonia

results than samples with coarser ammonium sulfate particles.

If the trendline expression overestimated the correlation of the LAR to the ISE results, the group is to the right of the trendline, and the particles would be coarser. The samples with coarser particles would not expose as much ammonium sulfate to the solution and the LAR results would be lower.

Future work

The promise of better correlation at higher sodium hydroxide concentration is unresolved. The presence or absence of the amines or hydrazine has not been made conclusively. Interference might explain the shift in results with the 25% testing solution. The testing solution may be found to dissolve all the ammonium sulfate from the sample.

The stirring time was set at 5 minutes as the practical limit for a fly ash marketer to get a result. Longer mixing time in an alkali solution of a hydraulic material could be problematic, but might have the benefit of working with more dilute testing solution and also reach the total dissolution of the ammonia in the fly ash.   Knowing the total ammonia content in the fly ash would make the determination of the ammonia in the concrete a mass balance of the constituents.

Samples for this work were taken without any information on the gas conditions in the exhaust stream. With this information a better explanation of the results might be possible.

An examination of the particles with an electron microscope and microprobe could determine the morphology of the ammonium sulfate particles in the fly ash.

CONCLUSIONS

The proximity objective was to find LAR testing conditions that resulted in values near to the values of the ISE result. The 1% sodium hydroxide testing solution at 20^0 C was closest to that objective.

The accuracy objective was to find the testing conditions that had the highest R^2 value and the best correlation to the ISE result. The single test results at 20% sodium hydroxide concentration and 50^0 C had a higher R^2 than any other testing solution.

The R^2 result in 10 repeats at 10% testing solution and 50^0 C were not as high as the single 10% test result and not as high as the 1% solution at 20^0 C.

The 1% testing solution at 20º C is less costly from a materials point of view, safer to handle, and sufficiently accurate to predict the ISE ammonia level quickly in a field lab setting.

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