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Use of Amonia Containing Fly Ash in Concrete

Arnon Bentur and Pavel Larianovsky
National Building Research Institute
Technion, Israel Institute of Technology

1. Introduction

The introduction of Selective Catalytic Reduction technologies for environmental control in the burning of coal in electricity producing plants has resulted in fly ash which contains ammonium. The source of the ammonium is ammonia in excess of the amount needed for the reduction of NO_x (called ammonium slip), which is deposited as ammonium sulfate on the fly ash particles.

In the alkaline environment which is developed in Portland cement concrete, the ammonium sulfate reacts with calcium hydroxide and ammonia gas is released. Studies have shown that the presence of the ammonium sulfate in the fly ash does not affect the properties of the concrete¹ and the main concern which should be addressed is the effects of the ammonia gas evolved, on the health hazards of labors involved in the production and placing of the concrete.

The object of the present study was to evaluate in the lab the extent of emission of ammonia gas from concrete with ammonia containing fly ash to serve as a quality control method which could provide indication whether there might be health hazards involved and develop guidelines for the limiting values on the ammonium content in the ash which would assure safe utilization in the concrete.

The present report deals with the development and running of the lab system. These lab tests are to be complemented by site tests to resolve to what extent the lab simulation is adequate for predicting the actual performance.

2. Experimental

The lab simulation is a modification of an experimental set up reported by Rathbone and Robl². It consists of a column (Figure 1) placed over a cylindrical mold (1 in Figure 1 and Figure 2), into which a 200mm thick concrete specimen is cast. Moist air is drawn over the concrete

¹ Koch and Prenzel, Tests on odour developments in the casting of a concrete screed using a NH₃ contaminated fly ash, Concrete Precasting Plant and Technology, issue 11, 1989

² R.F.Rathbone and T.L.Robl, A study of the effects of post-combustion ammonia injection on fly ash quality: Characterization of Amonia release from concrete and mortars containing fly ash as a pozzolanic admixture, University of Kentucky, 2001-2002

through the column at a controlled velocity through a system consisting of a pump, flow meter, valve and a trap, Figure 3. Measurements of the ammonia released over the concrete into the column is monitored by two different modes: (i) Direct measurement of the ammonia concentration in the column using a colorimetric tube (product of Kitagawa, Japan) which is inserted into the column (colorimetric method), and (ii) Measurement based on the standard exposure test of NIOSH 5015 which averages the ammonium concentration exposure over time, simulating respiration by human being, using a pump drawing air from the column into a tube which absorbs the ammonia (NIOSH method), Figure 4. The content of ammonia captured in the tube is determined later on by wet chemistry in a lab. On site such a system (pump + tube) is placed on a worker throughout the work period, between 2 to 8 hours. The direct measurement method (colorimetric method) provides the momentary concentration, while the NIOSH 5015 method provides average reading over the time interval during which the measurement is made. In a work place this is often the whole working day. In the current tests, intervals of 1.5 hours were taken to provide a profile of the change in the ammonia concentration emission over time.

Preliminary runs were carried out to set the air velocity in the system. The intention was to set a very low velocity to simulate in the lab harsh conditions. A velocity of 0.15 meter/minute was chosen, which is considered as almost stationary air.



Figure 1: Testing system for monitoring ammonia emission from concrete; (1) concrete chamber (see Figure 2), (2) pipe into which ammonia is emitted and monitored, (3) connection between concrete chamber and pipe using an O ring, (4) air inlet and bubbling through water, (5) connection to pumping system (see Figure 3)



Figure 2: Concrete chamber before assembly into the pipe and air inlet



Figure 3: Pumping system and traps: (1) (2) traps through which air containing ammonia is passed, (3) pump which draws air through the system, (4) flow meter and valve to control air velocity



Figure 4: Ammonia monitoring systems mounted on the column

Four series of tests were carried out. In the first two the effect of the source of ammonia was studied and the mixed concrete was cast into the mold immediately after completion of the mixing, at about 20 minutes; measurements of ammonia release in the column commenced thereafter. The third series explored the effect of prolonged mixing, simulating ready mix concrete operation while the fourth series evaluated the effect of high temperature, 40°C relative to the 20°C lab test.

In the first series, ammonia was introduced into the concrete by adding $\text{H}_8\text{N}_2\text{O}_4\text{S}$ salt, at a dose which would represent a contents of ammonia in the range of 2 to 100 mg/liter of mix water, which is the range expected in fly ash containing ammonia concretes². In this series the effect of air velocity was studied.

In the second series, fly ash having 180ppm of ammonia per kg was incorporated into the concrete, replacing cement at a 1:2 ratio, at contents 40, 80 and 120 kg/m^3 of fly ash.

In the fourth series the effect of processing, i.e. prolonged mixing simulating ready mix concrete operation was evaluated. The concrete was mixed for one hour before being cast into the mold. During the mixing period ammonia content in the air over the mixer was monitored; after placing in the mold and in the column the monitoring continued, but in the column, under the stream of wet air of controlled velocity.

In the fourth series, effect of temperature was explored by running the whole system in a climatic chamber at 40°C. All the tests of the first three series took place in a lab at 20°C.

The concrete studied in the third and fourth series were the ones having 80 kg/m^3 of fly ash, as the 80 kg fly ash mix in the second series.

The slump of all the concretes was in the range of 140 to 150mm. Their composition is provided in Table 1.

Table 1: Composition of the concretes

	Cement, kg/m^3	Fly ash kg/m^3	Water kg/m^3	Coarse aggregate kg/m^3	Medium aggregate kg/m^3	Fine aggregate kg/m^3	w/c ratio	W/b ratio
Reference	316	0	184	580	854	481	0.58	0.58
40 kg fly ash	284	41	193	557	821	516	0.68	0.59
80 kg fly ash	259	80	190	548	808	491	0.73	0.56
129 kg fly ash	240	120	190	549	808	473	0.79	0.53

The cement was type I and the fly ash was obtained from VGB powerTech at Deilbachtal 173, 45257 Essen-Kupferdreh, Germany. Special effort was made to obtain a high ammonia content fly ash to be able to run in the test a range of ammonia contents in the concretes. The ammonia content of the fly ash was 180 ppm and its chemical composition is provided in Table 2.

Table 2: Composition of the fly ash

Compound	Content, % wt.
Silica+ Alumina+ Iron oxide	89.82
Soluble phosphate, mg/kg	0.33
Alkalis as Na_2O	0.335
Cl	0.0025
SO_3	0.61
MgO	0.81
Free CaO	0.017
LOI	3.88
Moisture content	0.04

The concrete strength values at 28 days were 44.4 MPa for the reference 0.58 w/c concretes, and 39.6, 33.5 and 29.9 MPa for the 0.63 effective w/c ratios with 40, 80 and 120 kg/m³ fly ash, respectively.

The contents of ammonia per kg of mix water in the concretes is presented in Table 3. The expression of the ammonia content in terms of the ratio to mix water is based on conclusions by Rathbone and Robl² which showed that this seems to be the more dominant parameter controlling the value of ammonia emitted to the air from ammonia containing concretes.

Table 3: Amonia content in concrete calculated as mg ammonia per liter of mix water

Amonia source	Added salt	Added salt	40 kg flys ash	80 kg fly ash	120 kg fly ash
Amonia content, mg/liter mix water	2.2	22.3	33.6	67.3	100.9

3. Results and Discussion

3.1 Effect of ammonia content and source

The results of the first two series of tests are presented in Figure 5, with the source of ammonia being either salt added to the concrete mix or fly ash incorporated as partial replacement to the cement and the fine aggregate. In both cases a peak could be observed during the first few hours, while after 24 hours the ammonia emission was decayed considerably.

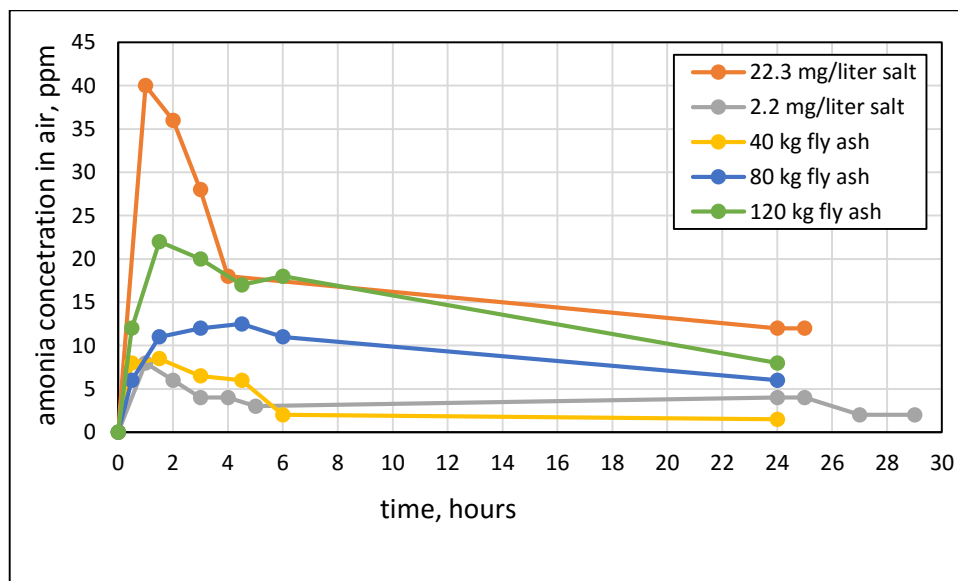


Figure 5: Amonia concentration in air measured by the colorimetric method

It can be seen that the peak of ammonia was much sharper when the ammonia source was the added salt, and also, the levels of ammonia emissions were much higher for the salt, as can also be observed when the peak emission is plotted against the ammonia content in the mix, Figure 6.

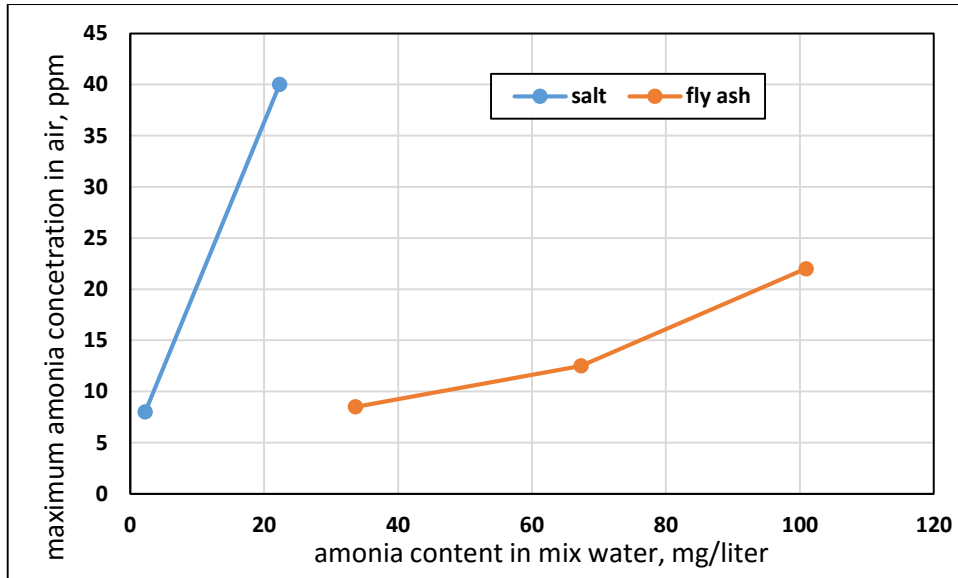
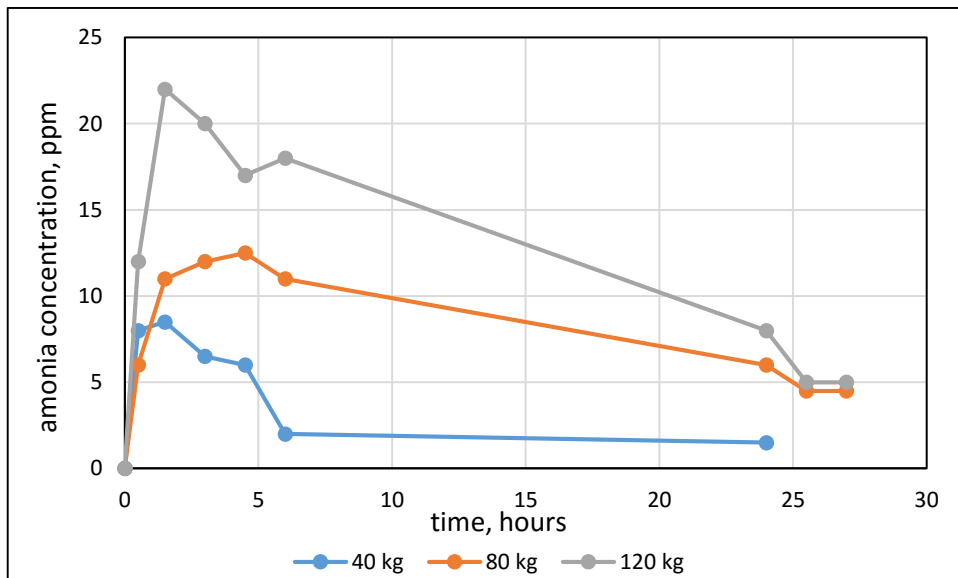
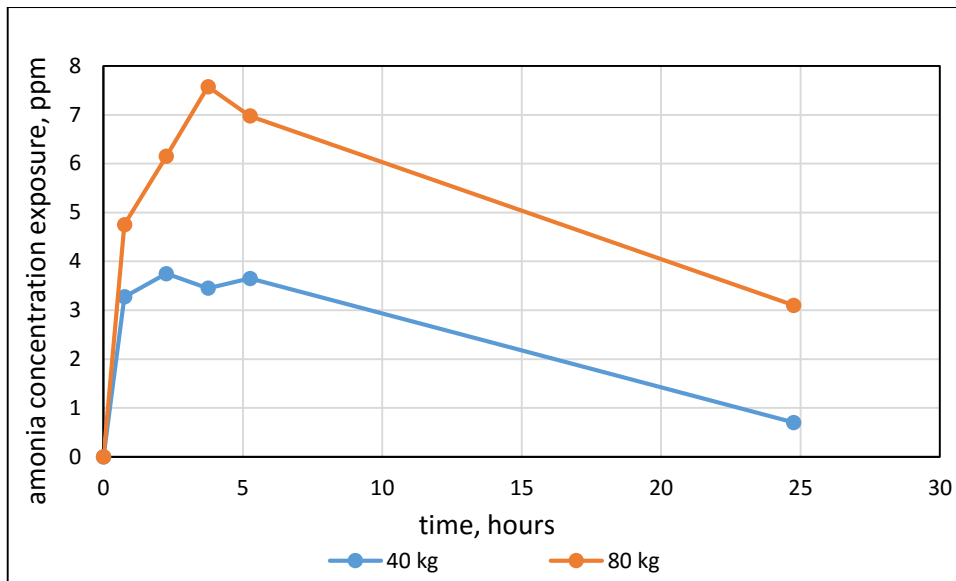


Figure 6: Ammonia concentration in air measured by the colorimetric method as a function of the ammonia content in the concrete and its source, salt or fly ash

The ammonia curves obtained by monitoring the emission using the NIOSH emission curves are presented in Figure 7a for the fly ash mixes. The trend is similar to that monitored by the colorimetric test tubes (Figure 7b), namely a peak during the first few hours which gradually decays towards 24 hours.



(b)



(b)

Figure 7: Ammonia concentration – time curves for mixes with fly ash, measured by the (a) NIOSH method, (b) colorimetric method

Although the trends are similar, it seems that the level of ammonia measured by the colorimetric tube (instantaneous measurement) is consistently higher than that obtained by the NIOSH method. This is clearly demonstrated in Figure 8, where the concentrations of the two tests are compared, showing a significant linear relation where the colorimetric test yields values which are higher by about 55%.

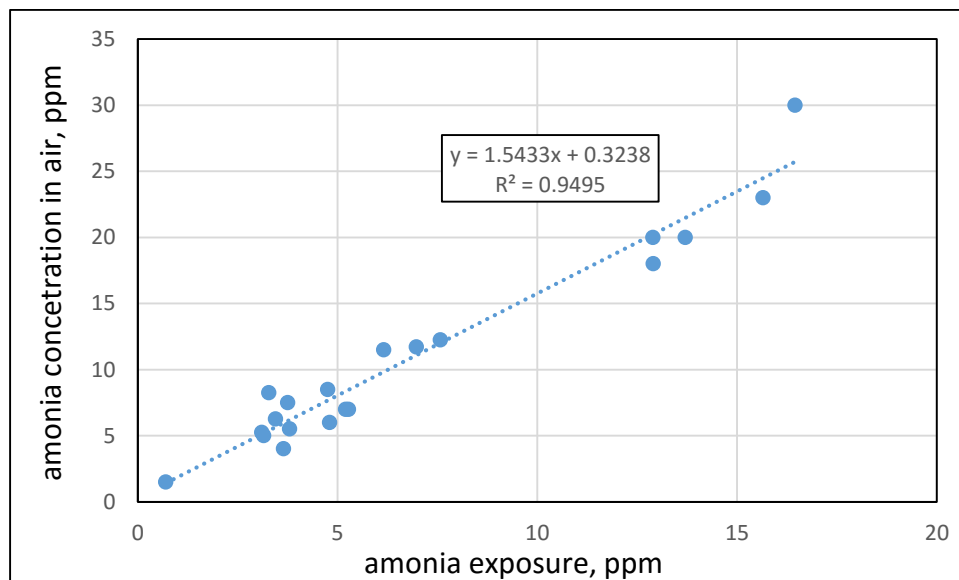
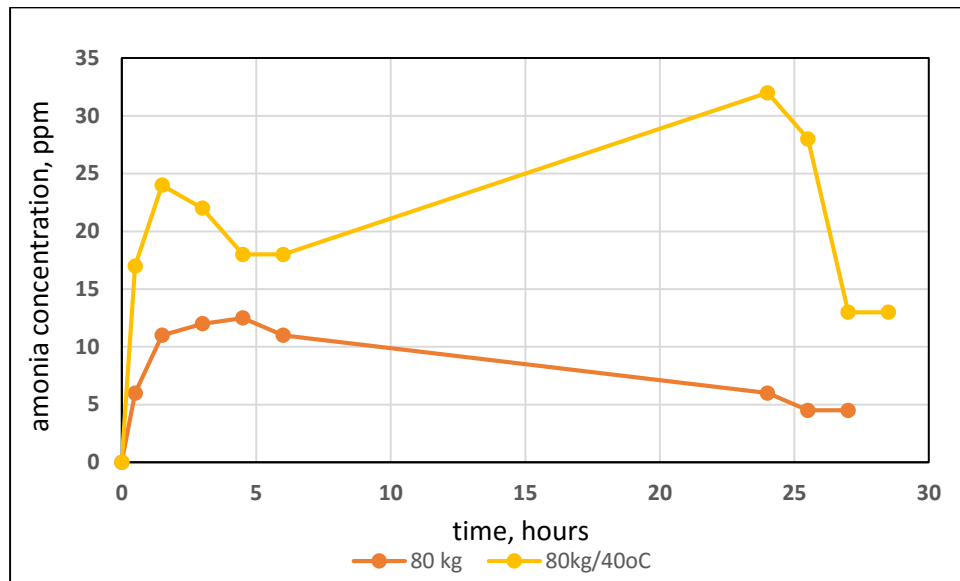


Figure 8: Relation between the ammonia concentration measured by the NIOSH method (ammonia exposure) and the colorimetric method (ammonia concentration in air)

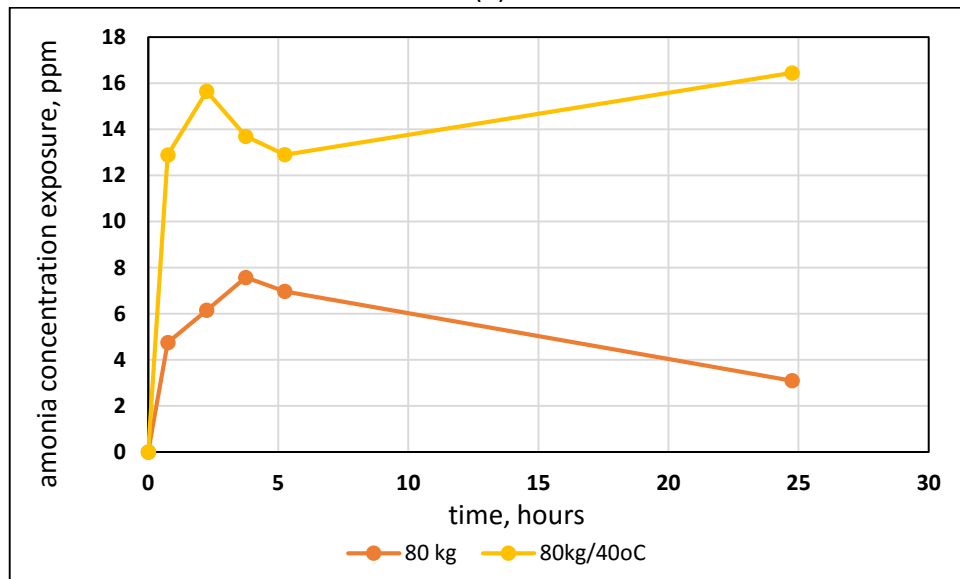
3.2 Effect of temperature

The effect of the temperature was obtained by studying the emission of a mix with 80 kg of fly ash containing ammonia at 20 and 40°C. For that purpose the whole set up was moved

from the 20°C lab to a 40°C climatic chamber, where the mixing as well as the emission monitoring were taking place. The results for the colorimetric and NIOSH monitoring are presented in Figure 9



(b)



(a)

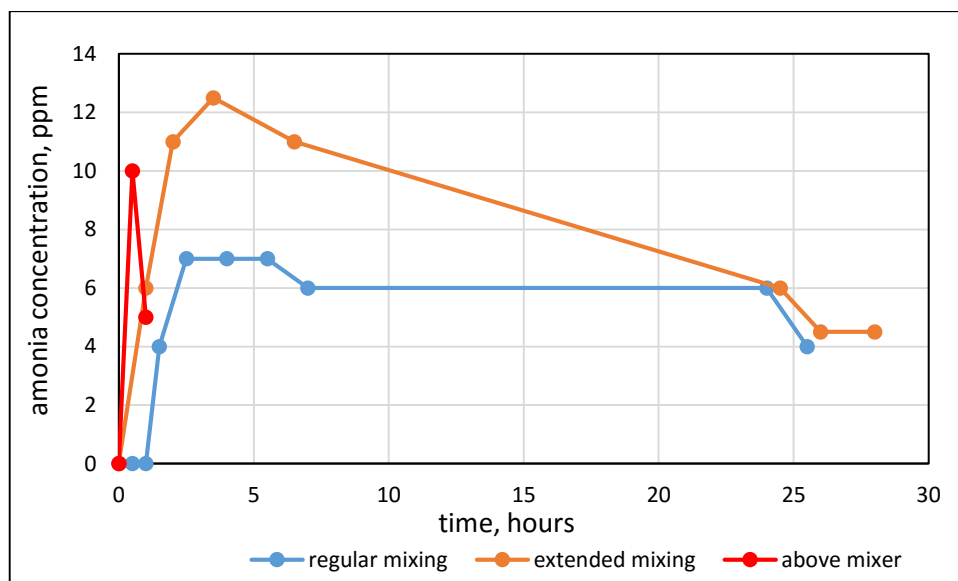
Figure 9: Effect of temperature on ammonia concentration – time curves for concrete mix with 80 kg fly ash measured by the (a) NIOSH method , (b) colorimetric method

The trends in the two monitoring systems are very similar: a peak during the first few hours at the two temperatures, but at 24 hours at the 40°C environment there seems to be a surge in the ammonia emitted which thereafter decays. This surge might be due to build-up of temperature within the column, due to the exothermic reaction of hydration which usually peaks after 8 to 12 hours. In the 20°C environment it may cool down but in the 40°C chamber the dissipation of heat is much slower. To verify this explanation a future test is planned which will include monitoring of the temperature within the concrete itself.

3.3 Effect of prolonged mixing

The tests reported in the previous sections represent lab conditions in which concretes are cast immediately after completion of mixing into the chamber representing a closed space. In practice, when ready mixed concrete is being applied, there is a need to take into account the influence of prolonged mixing in the truck, of about 1 hour, during which the concrete is continuously agitated in the open environment before being placed in a relatively confined space. This influence was simulated in this series of test in which the concrete was mixed for one hour in the lab in a free fall drum mixer, in a relatively open space, and thereafter cast into the pipe. During both time periods the ammonia release was monitored, during the first hour of mixing just above the free fall drum mixer opening, about 0.5 m above it, and thereafter in the pipe as in previous tests.

The results for the two periods are presented in Figure 10 and comparison is made with the previous lab series. During the first stage of mixing there is a sharp rise in the ammonia content, to levels which are similar to the peak obtained when the concrete is cast directly into the pipe after mixing. During the second stage, when the concrete after the prolonged mixing is cast into the pipe, the ammonia-time profile is similar in nature to that of the immediately cast concrete, namely a peak after the first few hours, but the levels of ammonia concentrations are lower. This behavior suggests that the ammonia emitted during the prolonged mixing comes on the expense of the ammonia which would have been emitted during casting.



(b)

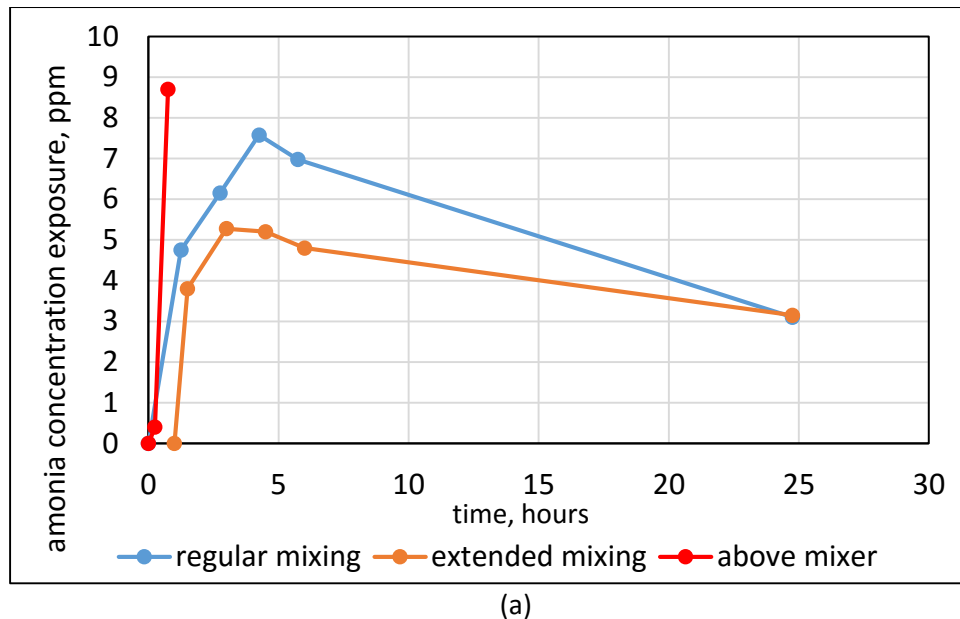


Figure 10: Effect of prolonged mixing on the ammonia concentration – time curves for concrete mix with 80 kg fly ash measured by the (a) NIOSH method, (b) colorimetric method

4. Conclusions

- The ammonia emitted from fly ash in concrete is smaller than the level obtained when a similar content is added directly as an ammonia containing salt. This probably reflects a dependency on the source of the ammonia, with the one coming from fly ash is less forthcoming with respect to discharge of ammonia gas.
- The trends of discharge of ammonia are similar when monitored by the NIOSH standard procedure and the colorimetric direct tests. Yet, the colorimetric test shows consistently values which are higher by about 50%. At this stage we have no explanation for this difference but the consistent trends and quantitative relations indicate that the colorimetric test which is easier to perform can serve as a reliable monitoring technique.
- The effect of temperature on the emission of ammonia is quite significant, resulting in doubling of the levels discharged when the temperature increases from 20 to 40°C. This increase however is smaller than expected on the basis of the rule of thumb that 10°C increase in temperature is associated with doubling of reaction rates.
- There is room to suggest that the test protocol conducted here represent conditions which would be harsher than the ones on field because of combination of several factors: almost stationary air velocity, confinement of the emitted gas in the column and smaller ability of dissipation of the heat build-up. To some extent this is verified by the results of the simulation of extended mixing. Further verification is expected to be obtained when the planned site tests will be carried out.
- It should be noted that in spite of the expected harsher conditions and the high level of ammonia in the ash, the level of ammonia concentration did not pass half of the threshold value recommended which is 25 ppm.
- The results of this lab study, when combined with the next phase of site studies could validate to what extent the lab procedures developed here could serve as quality control method with regards to ammonia release in concrete with respect to health hazards.