Research in Ammonia Diffusivity in Portland Cement Based Mixes

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ABSTRACT

Mortar and concrete are being tested to determine the ammonia diffusivity constants and how they change with age. Mortar (W:C + P = 0.485) with non-ammoniated class F fly ash added as a pozzolan is poured into 0.5-inch thick disks. Using the mortar to divide a sealed ammoniated chamber from a sealed natural-air chamber, the flux of ammonia through the disks is determined. With Fick's Law, this information leads to a diffusivity "constant" that diminishes as the mortar cures. One disk possessed a diffusivity of 2.8×10^{-8} m^2/s at two days old and dropped to 4.6×10^{-9} m^2/s by day eight. An older disk exhibited a diffusivity of 5.3×10^{-9} m^2/s at day eight. Further tests will attempt to show how easily ammonia can travel through concrete and mortar with different water-to-cement ratios.

INTRODUCTION

The use of SCR and SNCR systems in coal combustion creates unique problems in utilization of the ash. During the SCR process, ammonia is injected into hot ($315°$ to $400°C$) flue gases to form N_2 and H_2O in a catalytic reaction with titanium oxide substrate and active vanadium pent-oxide and other catalysts. The released water, along with water from other sources, reacts with this ammonia and sulfite (or SO_2 and O_2) to form ammonium sulfate and ammonium bisulfate. Some of these reactions are shown below:

$$NH_3 + H_2O + SO_3 ==> NH_4HSO_4$$
$$2NH_3 + H_2O + SO_3 ==> (NH_4)_2SO_4$$
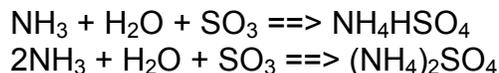
Both materials are associated with ammonia-slip deposits on ash—though ammonium bisulfate more readily deposits on ash particles (Golden 4-3).

It is possible to exploit ammoniated ash as a pozzolan in concrete with no adverse affects in strength or utility (Majors 2001). However, the ammonium

salts that cover the ash react in the high ph of the mix to release ammonia to the air. This ammonia release can cause problems to people who may be near the fresh concrete. In one case, fly ashes with 100-to-300 mg/kg ammonia were utilized in concrete experiments. During the pouring of concrete containing these ashes, unsafe levels of ammonia were recorded in the air (Brugghen 1995).

As concrete cures and ages, the pore-space within the mixture fills due to calcium carbonate precipitates and calcium-silicate hydrates. These "hydration products" bind the concrete constituents together (Dodson 1990):

Initially: Portland cement + H_2O ==> Calcium-silicate hydrates (gel) +$Ca(OH)_2$
Secondarily: $Ca(OH)_2$ + Pozzolan + H_2O ==> Calcium-silicate hydrates (gel)

 As these pores fill, the diffusivity of the concrete decreases. Therefore, ammonia remaining within the concrete or mortar emanates from the surface at lesser and lesser rates. An ongoing research project at the Center for Applied Energy Research at the University of Kentucky evaluates the rates of diffusion for ammonia through mortar and concrete disks.

The project seeks to quantify the changes in diffusivity that newly poured mortar or concrete undergo.

EXPERIMENTAL METHODS

Specimen preparation

For the mortar disks, a PVC ring-mold was fabricated. The mortar casts produced from this mold were 23 centimeters in diameter and about 1.3 centimeters in height. The casts possessed a volume of approximately 540 cm^3.

The mortar for the molds was mixed at a low water-to-cement ratio (W:C+P = 0.485) using ASTM-grade fine aggregate and ASTM grade 6 coarse aggregate for the concrete. Two liters of mortar were carefully mixed following ASTM C305 specifications with some modification during tamping that compensated for the small thickness of the disk compared to the diameter. The following charts show the general constituents for the mortar disks.

Mortar Constituents:

Cement (g)	429
Fly Ash (g)	107
Sand (g)	1475
Water (g)	260
W:C+P	0.485
Yield (L)	1

Some characteristics of the aggregate and fly ash used in the experiment are highlighted below:

C566

Test for Total Moisture Content of Aggregate by Drying

	Sand	Gravel
Ave % Moisture	4.4	0.07

C136

Sieve Analysis of Fine Aggregate

Sieve No.	% Passing	% Retained
4	96.8	3.2
8	83.4	16.6
16	72.7	27.3
30	54.7	45.3
50	13.4	86.6
100	1.8	98.2

Fineness modulus: 2.77

(Passes ASTM C33 standards for fine aggregate)

Ash analysis

ASTM C 618	
Item	%
Moisture	0.1
LOI	2.1
SO3	0.3
Si+Al+Fe	89.4
325	19.9

Chemistry	
Species	%
C	1.5
SiO2	54.5
Al2O3	6.6
Fe2O3	6.6
CaO	2.4
MgO	1.2
Na2O	0.4
K2O	2.5
NH3	N/A

Source: C.A.E.R. analytical lab

After mixing, the mold and mortar casts were placed into a humidified chamber for curing generally for one day. When ready, the mold was removed from the chamber and the cast was removed. The casts were then placed in an apparatus that enables us to determine the rate that ammonia passes through the concrete.

Experimental Specifics

The first three disks were made from mortar and the fourth disk from concrete. The coarse aggregate used in disk four was screened at about 1.27 cm (0.5") top-size. This was to keep the largest aggregate to disk thickness ratio at 1:3. This ratio should minimize any ammonia from traveling along the paste to aggregate interface for a significant distance, should this occur. In the trial with disk two, a small fan circulated air in the upper chamber. This was employed

originally to keep the upper chamber adequately mixed, and later became an experimental parameter that affected the results.

The disks were mixed to parameters outlined below.

Disk Specifics at Experiment Startup

	Disk 1	Disk 2	Disk3	Disk 4
Type	mortar	mortar	mortar	concrete
Age	14 days	24 hrs	24 hrs	24 hrs
Thickness	0.012m	0.012m	0.012m	0.036m
Area	0.030m^2	0.030m^2	0.030m^2	0.030m^2
W/C+P	0.485	0.485	0.485	0.543
[NH3] in source	1500ppm*	500ppm	500ppm	500ppm
slump	N/A	N/A	N/A	2.5 "

Test apparatus

The ammonia measuring apparatus consists of a two-chambered unit separated by a disk of mortar (or concrete) modeled after a similar test by Houst and Whittmann (1994); which measured oxygen and carbon dioxide diffusion through concrete. These previous tests utilized a constant flow of gas through the cells. In this ammonia test, the chambers were sealed with vacuum grease, gaskets, and clamps. The bottom chamber held a beaker of ammoniated solution at high ph. In order to achieve a similar humidity in both compartments, the top chamber contained a suspended saturated sponge while the bottom chamber utilized the source beaker of ammoniated water to humidify the air. Figure 1 gives a better idea as to the construction of the apparatus.

An ammonia gas-sensing electrode provided the means to measure the concentration of gas in the upper chamber. The lower chamber's ammonia concentration could then be calculated from this information.

The test

Determination of diffusion coefficient with this apparatus is possible with Fick's Law:

$$\frac{dm}{dt} = -\frac{S \, D \, dc}{dx} \qquad \text{or} \qquad J = -\frac{D \, dc}{dx}$$

where *dm/dt* it the number of moles flowing through the membrane for unit time and *S* is the cross sectional area. *J* is the flux of the gas in question per cross

sectional area of the membrane (in this case, a porous mortar disk). *D* is the diffusivity of the gas, *dc* the concentration change (*c1-c2*) and *dx* the thickness of the disc (*l*).

Fig 1: Break-a-way diagram of diffusion experiment.
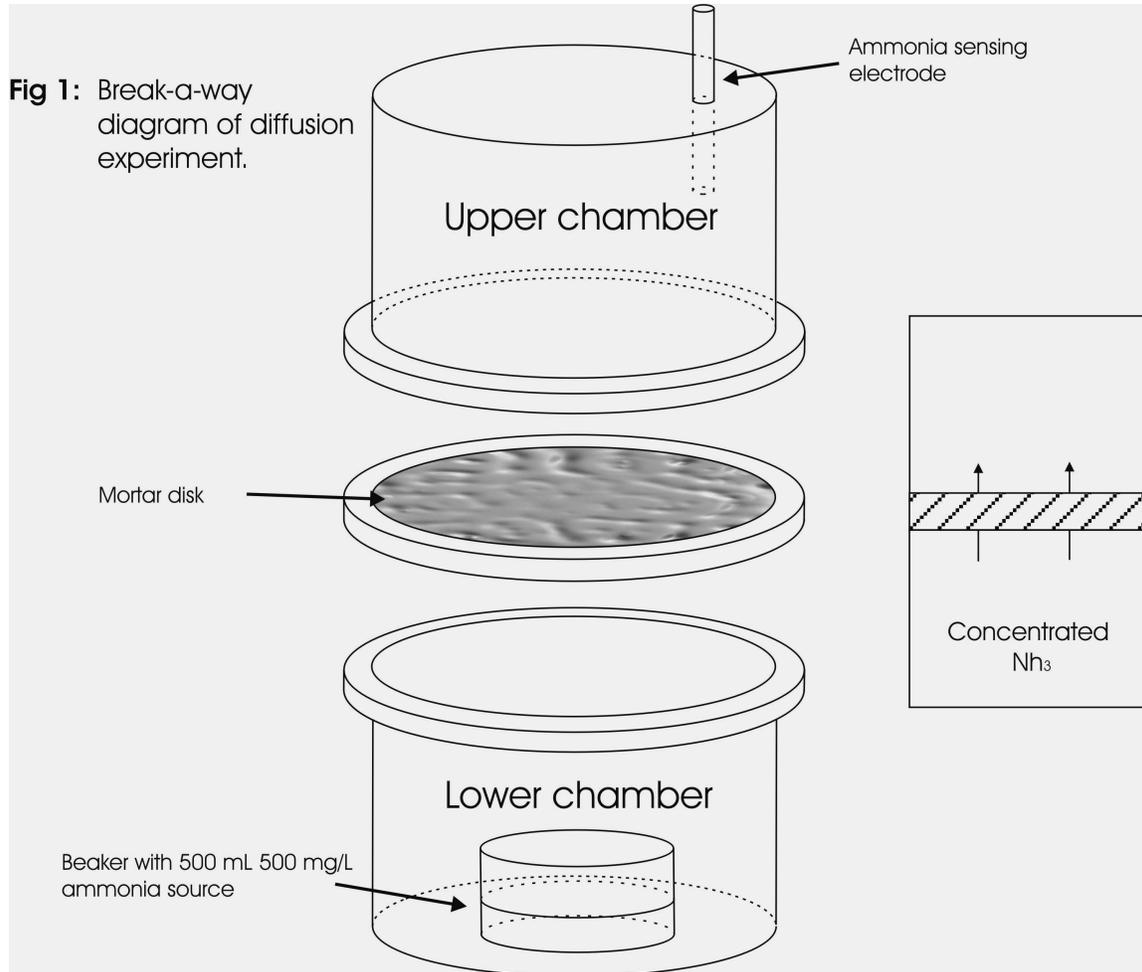
To measure the diffusivity (D), we need to find the ratio of flux to the concentration changes in the two chambers. D is measured in meters^2/sec, *J* in moles/((meters)^2*seconds), *l* in meters, and *c1-c2* in mols/(meters)^3:

$$J = -\frac{D\,(c1 - c2)}{l}$$

and therefore

$$D = -\frac{J\,l}{c1 - c2}$$

With D calculated, we can evaluate how the diffusivity in the cementitious mix changes over time.

DISCUSSION

Results

The raw data produced by the ammonia-sensing electrode is illuminated below. Note the rate of concentration change slows as the difference in concentration between the two cells lessens. Disk one does not show this within the time frame because the source ammonia concentration was three times higher and possible pressure differences. The lower chamber was fed by tank instead by the typical ammonia source flask used in the other three trials recorded. The concentrations obtained are noted below (in mg N/kg air):
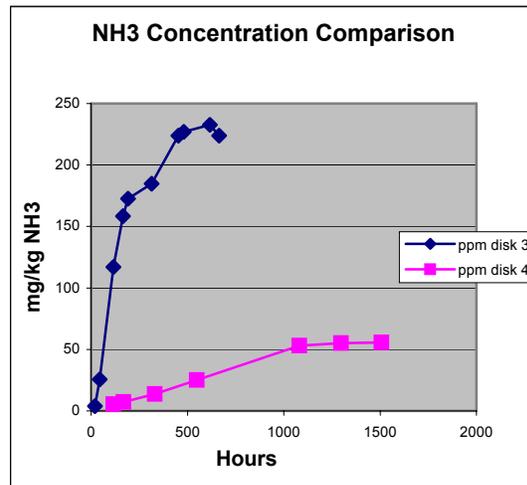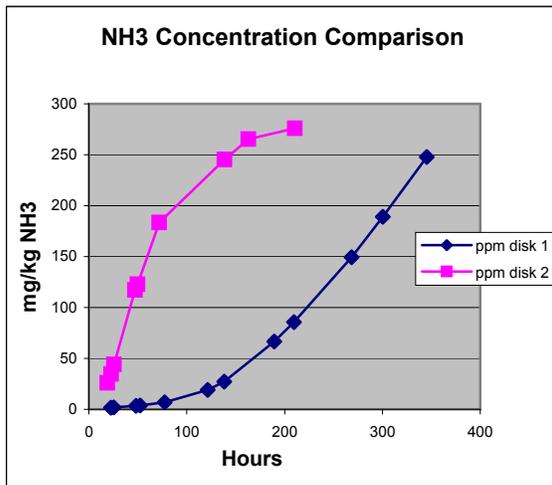
The calculated Fluxes (J) within the same time frames are as follows:
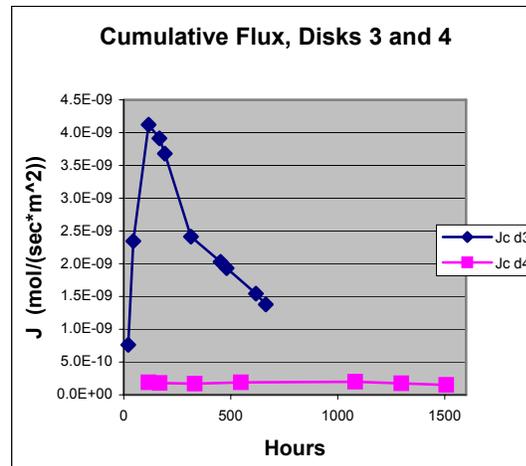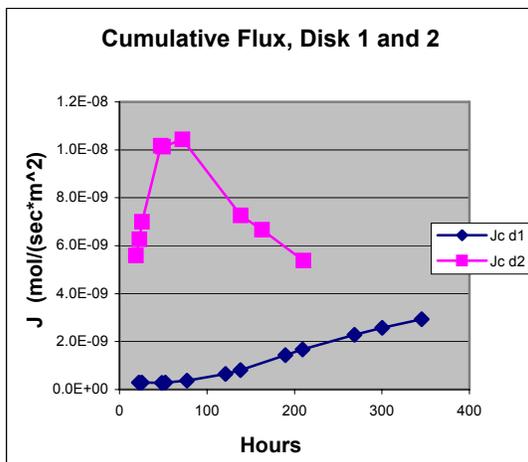
Flux changes began with a "ramping up" period to a steady state. This is especially apparent in the results in disk 1 and 3. Though disks 2 and 3 were of similar setup, the results obtained are somewhat different. This probably

resulted from the presence of the fan in the upper chamber. Air movement may have caused minor pressure changes on the disks upper surface, or served to remove ammonia from the disk surface layer faster.

The diffusivity "constant" changes almost in a linear fashion to the trends observed in the flux. The following graph shows how the diffusivity of the 4 disks changed.

A snapshot of the diffusivity constant during similar timeframes is listed below:

	Disk 1	Disk 2	Disk 3	Disk 4
50 hrs	1.23E-09	2.88E-08	1.18E-08	2.57E-10
100 hrs	2.63E-09	2.53E-08	1.53E-08	5.14E-10
200 hrs	1.11E-08	4.56E-09	6.60E-09	4.71E-10
500 hrs			1.29E-09	6.39E-10

Where D is m^2/sec

Conclusion

Ammonia diffused through the thicker concrete disk far slower than the thinner mortar disks. More experimentation is needed to see if this is a result of aggregate-matrix reactions or the result of an experimental anomaly. Further work is already underway to evaluate this phenomenon. Also, all disks, after an initial ramping up period, experience a dramatic drop in diffusivity within the first 200 hours (8-9 days). This suggests that after one or two weeks, ammonia diffusion through mortar will drop by a factor of ten. More work is needed to see what effect time has upon the diffusivity of concrete.

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