

Application of Glass Corrosion Tests to the Reactivity of Fly Ash

**Walairat Bumrongjaroen¹, Isabelle Muller¹, Jeffrey Schweitzer²,
Richard A. Livingston³**

¹ Vitreous State Laboratory, The Catholic University of America, 620 Michigan Ave., NE, Washington, DC 20064; ² University of Connecticut, 2152 Hillside Road, Storrs, CT 06269; ³ Office of Infrastructure R&D, HRDI-05, Federal Highway Administration, 6300 Georgetown Pike, McLean, VA 22101

KEYWORDS: fly ash, pozzolanicity, reactivity test, glass corrosion, leaching

ABSTRACT

Comparison among several tests for measuring fly ash pozzolanicity has been made in this study. Indirect tests based on measurement engineering properties of mortar or concrete may be not useful for understanding these mechanisms because of the additional factors of aggregate and cement properties. Direct tests which concern only fly ash could be applied instead. These methods characterize various aspects of the corrosion process including ion leaching, hydration profile development and dissolution. They involve exposure to water under different conditions such as flow through or static closed system, and elevated temperatures. Each combination has advantages and disadvantages, and not all combinations have been evaluated yet. The tests adopted from standard methods for nuclear waste glass such as Vapor Hydration Test and the Single-Pass Flow Through Test were conducted. Preliminary test results suggest that the silica, alumina, and calcium uniformly are leached out after early leaching of sodium. Nuclear Resonance Reaction Analysis was also applied to observe the ion exchange processes within the glass on a nanometer scale. Finally, the models for incorporating the reactivity result into proportioning cement/fly ash mixes were reviewed.

I. INTRODUCTION

The reactivity of a given fly ash is a critical factor in the design of concrete mixes using it. Despite this fact, there is much uncertainty about how the reactivity is defined or measured. In general, there have been two major approaches to fly ash reactivity tests: direct and indirect. The indirect tests such as ASTM C-311¹ involve mixing the fly ash with Portland cement and aggregate, casting bars or cylinders and then measuring some macroscopic property such as compressive strength, expansion or permeability. This approach introduces many more variables such as the particle size-distribution and chemical composition of both the Portland cement and the aggregate, This makes it difficult to evaluate the reactivity of the fly ash itself².

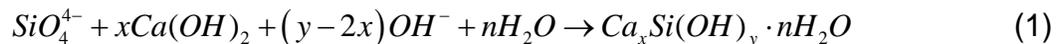
In contrast, the direct tests concern only the fly ash. However, this still involves several factors that affect reactivity including particle size distribution, glass fraction and the

glass chemical composition. In principle, the first two factors can be measured independently. The third factor, glass chemical composition, determines the thermodynamic driving force of the reaction. It also influences the kinetics through the formation of various types of surface layers that can control the rate of reaction. These aspects have been studied extensively in the field of glass corrosion. The objective of this paper is to apply these concepts to develop a better understanding of the fly ash reactivity tests.

Fly ash is a member of the class of pozzolanic materials. However, there is some ambiguity about the definition of pozzolanic action. According to ASTM C593 a pozzolan is a "siliceous or aluminosiliceous material that in itself possesses little or no cementitious value but that in finely divided form will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or assist in forming compounds possessing cementitious properties"³. This essentially defines in terms of indirect test.

A more direct definition is given by Mehta and Monteiro (2006) is that a pozzolanic material reacts with calcium hydroxide to form a reaction product that is similar in composition and properties to C-S-H⁴.

The pozzolanic reaction can thus be written as:



where the silicate ion is supplied by the pozzolanic material, and the calcium has to be added in the form of calcium hydroxide. In a Portland cement/ pozzolan mixture, this comes from the excess Ca remaining from the main C₃S hydration reaction. The C/S ratio represented by x for C-S-H is about 1.65 for the pH range usually found in concrete

Equation 1 suggests several approaches to developing fly ash reactivity tests. For the reactants, one can measure the rate of supply of silica to the solution or the consumption of CH. On the right-hand side, one can measure the amount of C-S-H gel that is produced. Since the reaction is exothermic, it is also possible to measure the heat of hydration. All of these approaches have been tried and they are discussed below, but first it is necessary to consider how the properties of the glass affect the kinetics of the reaction.

II. RATE CONTROLLING MECHANISMS

The overall hydration reaction of fly ash glass is quite complicated because the glass is not a simple binary compound, but contains several additional constituents such as alkalis and aluminum. Moreover, silicate chemistry itself is complex.

The mechanisms involved in the pozzolanic action of glassy fly ash can be separated into three mechanisms: (1) Rapid ion exchange of alkalis in the glass with H₃O⁺ ions

from the solution, 2) Dissolution of the silica network, 3) Precipitation of secondary phases on the glass surface. Assuming that the glass and solution form a closed system, different mechanisms dominate at various stages of the reaction as shown in Fig. 1

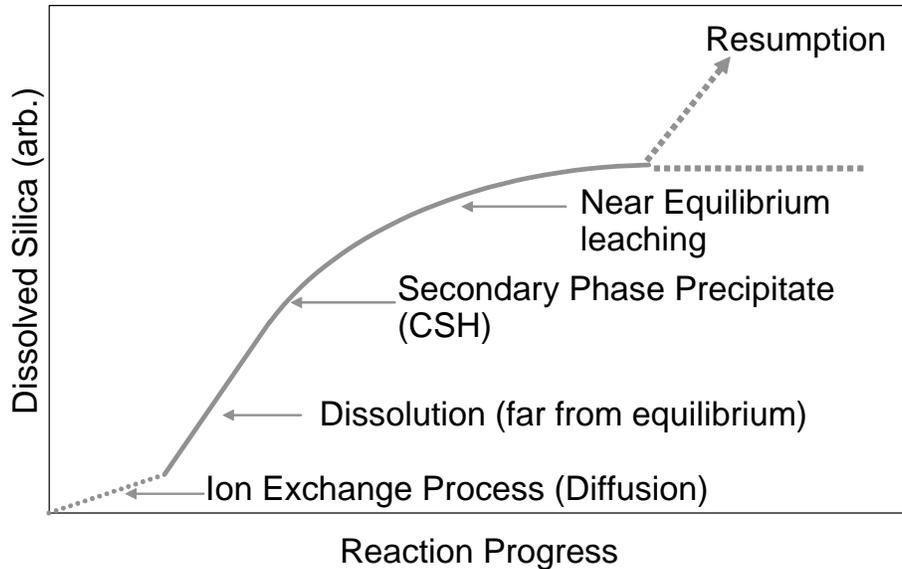


Fig. 1: Evolution of Leaching Mechanism of Glass Hydration in a Closed System

These leaching mechanisms are influenced by the glass matrix itself, various surface layers, and the solution chemistry. The effect of glass composition is prevailing when the concentration of species in solution is far from equilibrium. Its effect depends on how the chemical species incorporates in the network structure.

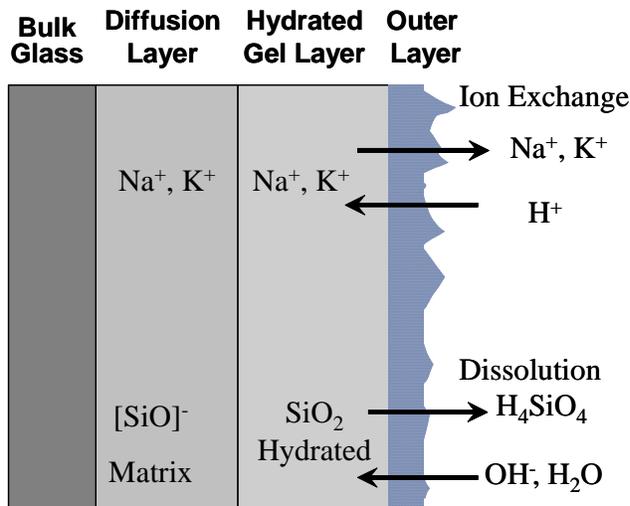


Fig. 2: Schematic diagram of glass hydration surface layers

The leaching of glass is influenced by surface layer. As shown in Figure 2, the surface layer consists of a diffusion layer inside the glass, the gel layer between the diffusion layer and the precipitated layer which is the outermost layer. When the concentration of element in the solution reaches their saturation level, this promotes the formation of secondary phase which may precipitate back to the surface. This layer can inhibit the mass transport through the surface layer. When the concentrations of element in solution are near saturation, the effect of solution is dominant.

III. REACTIVITY TEST METHODS

As noted above, a number of approaches can be used as the basis for fly ash reactivity tests. Table 1 summarizes the leaching tests. This includes standard tests developed for nuclear waste glass corrosion along with others developed specifically for fly ashes or alkali-silica reaction. Some of the methods listed such as small angle neutron scattering (SANS) and inelastic neutron scattering (IENS) can only be done at specialized facilities. However, they can serve as reference methods to calibrate and to characterize the fundamental processes controlling reactivity in order to refine other, simpler methods that can be used in a local construction materials testing laboratory.

Table I: Reactivity test Methods

	MEASURAND	ANALYTICAL METHOD	REF.
1	Dissolved silica	Wet chemistry, ICP-AAS	5;6;7; 8
2	Conductivity	Electrical conductance	9; 10; 11; 12; 13; 14
3	Heat of hydration	Calorimetry	15; 16; 17
4	CH consumption	XRD, IENS, Thermal analysis	18; 19; 20; 21; 22
5	Hydration layer depth	NRRA, SEM	23 24
6	Gel surface area	SANS	25; 26
7	Gel volume	Osmotic Pressure, Ion Exchange, Acid-base	27; 28

Table I has columns for measurand and also for the analytical technique. This emphasizes the fact that a given measurand may be measured by more than one technique. However, in many cases the results from these different methods may not be completely comparable.

1. Dissolved silica

There are a number of standard wet chemical techniques for measuring dissolved silica (or in some cases another ion of interest). Ion-coupled plasma Atomic Absorption spectroscopy and related methods are relatively rapid and precise methods for determining the total amount of a given element. However, this method cannot give concentrations of individual ionic species, which may be critical for determining it if the solution is saturated with respect to various phases.

At low or neutral pH, dissolved silica is a reasonably accurate measure of the actual amount of leached silicate. However, as discussed above, at $\text{pH} > 10$ the silicate tends to form a gel. In this situation, dissolved silica alone would tend to underestimate the actual amount of leaching. Consequently it is necessary to consider tests that quantify the amount the gel itself as described below.

2. Electrical Conductivity

The conductivity of a solution can be measured conveniently and very precisely. Therefore, Many researchers have attempted to apply it to monitor the pozzolanic activity of fly ash^{9;13;11:10; 12:29}. The assumption is that the conductivity is dominated by a single ion such as Ca which correlates with the progress of the pozzolanic reaction. However, as Hellmuth (1987) points out the solutions in contact with fly ash tend to have complex chemistry that may confound the measurement²⁰.

3. Heat of Hydration

Other researchers have used the heat of hydration to follow the progress of the pozzolanic reaction of fly ash^{16;17:15}. However, the observed heat of hydration represents the sum of all the simultaneous endothermic and exothermic reactions, and thus may not truly reflect the main pozzolanic reaction.

4. Calcium hydroxide consumption

Since $\text{Ca}(\text{OH})_2$ is a major reactant in pozzolanic reactions, test methods have been sought to characterize the pozzolanicity of materials in terms of $\text{Ca}(\text{OH})_2$ consumption^{18; 20}. This in turn requires a method of quantifying the amount of $\text{Ca}(\text{OH})_2$ present as the reaction continues. The most commonly used direct methods are wet chemistry, thermal analysis and X-ray diffraction. Each measures a somewhat different component of the $\text{Ca}(\text{OH})_2$ present.

4.1 X-ray diffraction (XRD): One drawback with XRD is that it measures only the well-crystallized portlandite phase, but it is known that there is also cryptocrystalline $\text{Ca}(\text{OH})_2$ occluded in the C-S-H gel¹⁹. Thus, the measured amount may not reflect the total amount of CH consumed by fly ash. Also, to obtain accurate quantitative results, extensive sample preparation is required. Another drawback of XRD is that they are all destructive, so it is not possible to follow the reaction over time in the same sample.

4.2 Inelastic Neutron scattering (IENS): This method uses neutrons to probe the resonant frequencies of interatomic bonds involving hydrogen. It has been applied to make *in situ* measurement of the amount of calcium hydroxide in cement paste samples^{30 31}. The nondestructive nature of the technique makes it possible to remeasure the same specimen over time and thus to determine the kinetics of the pozzolanic reaction. A drawback is that it can only be done at a special nuclear facility. Nevertheless, since it is very precise and does not require empirical calibration factors, it is useful as an independent reference method.

5. Hydration Layer Depth

As shown in Fig. 2 the pozzolanic reaction results in an alteration of the original material into a hydrated layer, and the depth of the layer can thus be correlated with the progress of the reaction. This hydration layer can be visualized by SEM on cross sections of the sample that have been cut normal to the surface. This would not be possible on individual fly ash particles, but it can be done on synthetic glass samples with compositions similar to fly ash glass. Consequently, it may be useful as a reference method.

5.1 Nuclear Resonance Reaction Analysis (NRRA): This method has the unique capability of measuring hydration depth without sectioning the sample. It is an ion beam technique that uses the resonance capture of ^{15}N ions by hydrogen to measure the depth profile of hydrogen below the surface of a hydrated specimen^{24;24}. The shape of this profile can be interpreted to derive information about surface layers and diffusion processes within the glass.

6. Gel Surface Area

Gels are fractal materials and thus its surface area also provides information about its volume. Small angle neutron scattering (SANS) has been employed by many researchers to characterize the Portland cement gel and pore nanostructure^{32; 33}. In the SANS system, intense collimated beam of neutrons is passed through the sample in which scatters out of the incident beam direction by interactions with features inside the structure. It can be used to determine size distributions and volume fractions of microstructural features, fractal components within the microstructure, and the total surface area.

This technique can access the surface area of all particles inside the cement structure which other techniques such as BET or mercury intrusion techniques cannot access.. In addition to the gel morphology, the technique can determine how the hydration products, C-S-H gel, are distributed in the paste. It makes use of different length scale to distinguish the fractal in the pore solution and the fractal deposited on the large particles such as cement grain and fly ash. The ratio between these two types (S_{vf}/S_{sf}) can be used as a measure on how the hydration products are distributed. Ideally, the highly reactive system would yield high ratio of volume fractal to surface fractal. The same group has applied the SANS technique to investigate the microstructure development of fly ash cement paste system through the distribution of these two fractals. A disadvantage of SANS is that it can only be performed at special nuclear facilities.

7. Gel Volume

The gel can be a combining product of hydration process and pozzolanic action. The pozzolanic activity of fly ash can be determined by quantifying the C-S-H gel amount. To date, there is no chemical analysis test which can directly quantify the actual volume of C-S-H gel. This might be owing to the variation in stoichiometry of the gel. Two tests are investigated in this study to directly measure the actual volume of gel; Osmotic Pressure Test and Ion Exchange method.

7.1 Osmotic Pressure Test: A simple method that effectively measures the volume of the gel is based on osmotic pressure. As discussed above, gels possess enormous surface because of their fractal nature, and a significant amount of pore water molecules become adsorbed on this surface. This reduces the activity of the solution below the value of one for pure water and thereby changes the osmotic pressure. It can be measured by enclosing the sample containing gel in a semi-permeable membrane. This is then immersed in a bath of known activity. Water exchanges across the membrane until the two solutions are in equilibrium. The change in the osmotic

pressure of the bath is thus a measure of the original osmotic pressure of the sample. An osmotic cell test was developed by Verbeck and Gramlich for alkali silica reactivity of aggregates³⁴, and subsequently modified by Stark and Schmitt²⁸.

7.2 Ion Exchange: Another approach to the measurement of gel volume would be a modified version of gel column ion chromatography. In this application, the standard silica gel beads would be replaced by the fly ash particles, which would be reacted with a solution of fixed chemistry under flow through conditions for a specified time interval. Then a solution containing a known concentration of an ion with an affinity for the gel would be pumped through the fly ash column. For example, uranyl acetate is a well known method for detecting alkali-silica reactivity because of the high affinity of uranium for silica gels. The difference in the exchange ion concentration between the inlet and the outlet would be a direct measure of the amount of gel formed on the fly ash.

7.3 Acid-Base Leaching: Several tests have been developed that use a strong acid or base to attack the soluble silica in the gel, but not the silicate in the unreacted fly ash. The dissolved silicate is then determined by one of the analytical methods described above. The success of the method depends upon the choice of an acid or base and the contact time that maximizes the dissolution of the silica in the gel and minimizes the attack on the silica in the substrate.

IV HYDRATION CONDITIONS

In addition to the choice of measurand, and analytical method in the design of reactivity, there is also a set of options for the hydration conditions, i.e. flow conditions, solution chemistry and operating temperature, that need s to be considered. Most conventional fly ash reactivity tests have been batch tests in which a fixed amount of solution is mixed with the fly ash and the reaction proceeds in a closed system under room temperature. In contrast, for the investigation of nuclear waste glass durability a number of test methods using different hydration conditions have been developed. These are listed in Table II.

Table II: Nuclear Waste Glass Hydration Procedures nuclear waste glass

Name	System	pH	Water State	Temperature °C
PCT	Closed	Floating	Liquid	90
VHT	Closed	Floating	Vapor	200
SPFT	Open	Fixed	Liquid	35-90
Soxhlet	Open	Floating	Liquid	90-100

1. Product Consistency Test (PCT)

PCT is a static leaching test designed to simulate near equilibrium condition or long term leaching³⁵. This batch test was originally designed to determine the dissolution of radioactive species leaching from waste glasses. The standard PCT uses distilled water for the starting solution. However, the high temperature enhances the leaching process by increasing the diffusion rates and reaction rates of the glass constituents.

2. Vapor Hydration Test (VHT)

The vapor hydration test is a means of modeling the long-term corrosion behavior of glass in contact with water vapor³⁶. In the test, a monolith sample is exposed to water vapor in sealed vessel. At 80% humidity, a thin film of water condenses on the glass surface corroding the glass. The corrosion process is accelerated by using high temperature of 90 °C. It is an accelerated static leaching test that is designed to simulate near equilibrium condition. The conditions are static, closed system and high temperature. The drawback is that the chemical species in the solution cannot be controlled and measured. The hydration occurs from the reaction between water vapor on surface of glass specimen.

3. Single-Pass Flow Through Test (SPFT)

Single-Pass Flow Through test is a continuous flow system⁷. The test varies the flow rate of leachant to the glass containing chamber. At high flow rate, the precipitation of the secondary phase is minimized. It allows monitoring of the concentration of dissolved species, analysis of the effects of the flow rate and solution composition and characterization of the intrinsic reactivity of glass. The system maintains uniform pH and to fix the reaction affinity at a high level. Typical measurand is the normalized mass loss of major compound in glass such as Si.

The test condition is designed to obtain the far from equilibrium condition which prevents the formation of secondary phase. The test accelerates the leaching process by using high temperature and high S/V. The system is performed under controlled conditions of constant pH, temperature and solution composition. It can be used to determine the free silica in the glass or can be used to investigate the factors controlling dissolution process of glass. The test can be performed with either continuous or periodic refreshment of leachant and removal of the leachate from the system.

4. Soxhlet

This approach, which is widely used in chemistry, is a hybrid. It is a closed system in the sense that the total volume of water remains constant, but the solution that comes into contact with the solid reactant has the constant chemical composition of pure water. Thus it also has aspects of an open system. The apparatus has three components. In the reaction chamber the solution flows over the solid reactant. It then passes into an evaporation chamber. The resulting vapor rises into a condenser, and the resulting distilled water is then recycled back through the reaction chamber. The apparatus is arranged with the evaporation chamber below the reaction chamber and the condenser approach so that the circulation of the solution is driven by gravity and no moving parts are required. Its temperature is near boiling water temperature.

V. CASE STUDIES

In order to investigate the performance of different combinations of hydration conditions, measurands and analytical methods, some studies were made using specially prepared fly ash materials. In one case synthetic fly ash glasses were used. In the other the fly ash was separated into a series of density fractions using centrifuging.

1. Synthetic Fly Ash Glasses

It is difficult to work with actual fly ash samples as standard test materials because of limited compositional ranges, varying inert fractions and particle size effects. Therefore glass samples with compositions similar to those of fly ash were made^{37; 38}. Two series of CAS glasses were prepared from mixtures of the oxides SiO₂, Fe₂O₃, Al₂O₃, Na₂O, CaO, MgO, and K₂O³⁹. Two different hydration methods, SPFT and VHT, were used, and the main analytical method was ICP_AAS for dissolved ions. NRRRA was also applied to learn more about the formation of surface layers.

1.1 SPFT: Powdered samples of the synthetic fly ashes were immersed in a strong LiOH, pH > 12.5, solution for 28 days, and the concentrations of Si, Al, Fe, Ca, Mg, Na, and K in the solution were monitored daily for 28 days. Some of the results for the SPFT test are shown Figs. 3a and 3b as plots of the normalized mass losses of Si over time⁴⁰. Since there was no difference in particle size or inert fraction between these two types of glasses, this demonstrates that chemical composition is definitely an important factor in fly ash reactivity.

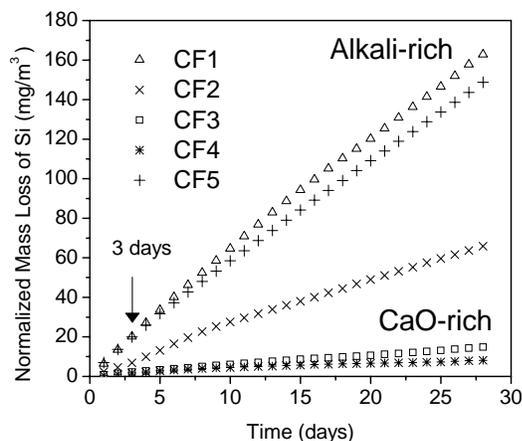


Fig. 3a Normalized mass loss of Si for CF Series in pH 12.5

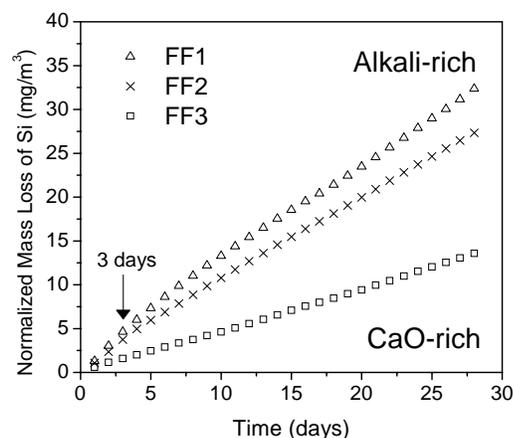


Fig. 3b Normalized mass loss of Si for FF Series in pH 12.5

The results show an order of magnitude difference between the two series. FF glass with a high ASI value yields lower Si leaching rate than CF glass. These effects can be explained by the fact that most of the alkalis are bound with alumina tetrahedral resulting in less alkali left in the NBO sites for the ion exchange process. Since ion exchange is a controlling mechanism for glass leaching at early stages, low alkali mobility would decrease the leaching rate significantly. Consequently, higher alumina contents, as in the case of the F-type glasses would inhibit Si dissolution. In addition to the differences in dissolved Si between the two types glasses, within each type there is a trend of higher dissolved Si going from the Ca-rich to the alkali-rich members. It is also found that the glasses with higher excess alkali content from charge balancing have higher leaching rates in the ion exchange process. These glasses are leached at high constant rates indicative of network dissolution stage. In contrary, a glass with high

calcium content such as CF3 has a low leaching rate approaching equilibrium. The leaching of Si may be inhibited by a lower ion exchange rate or by the formation of a condensed gel layer. Other evidence for the presence of this layer will be investigated in the following section.

1.2 NRRA: This analytical method requires a monolith sample with a smooth flat surface. The monolith was hydrated in a LiOH solution (pH 12.5) for a period of 72 hours. Then all were removed from solution, treated with pure methanol to stop the reaction and placed in a vacuum chamber until analyzed with ^{15}N beam.

Examples of NRRA hydration depth profiles are shown in Fig. 4 for the glasses CF2 and CF3. These profiles cover a depth range of approximately 1.5 microns. Since all the specimens were hydrated for the same amount of time, the area under the curve is a crude measure of the reaction progress. At depth, the amount of hydrogen is greater for CF2, which is consistent with the greater amount of leaching observed in the previous Si leaching curves. However, at the surface the concentrations of hydrogen are reversed, and there is a Gaussian peak in the CF3 profile that is characteristic of a hydrated surface layer. This suggests that there may be enough calcium available in this glass to react with the silica to form a C-S-H type gel within the hydrated layer. In contrast, for CF2 there is no surface layer and instead the curvature of the profile suggests a much more open structure.

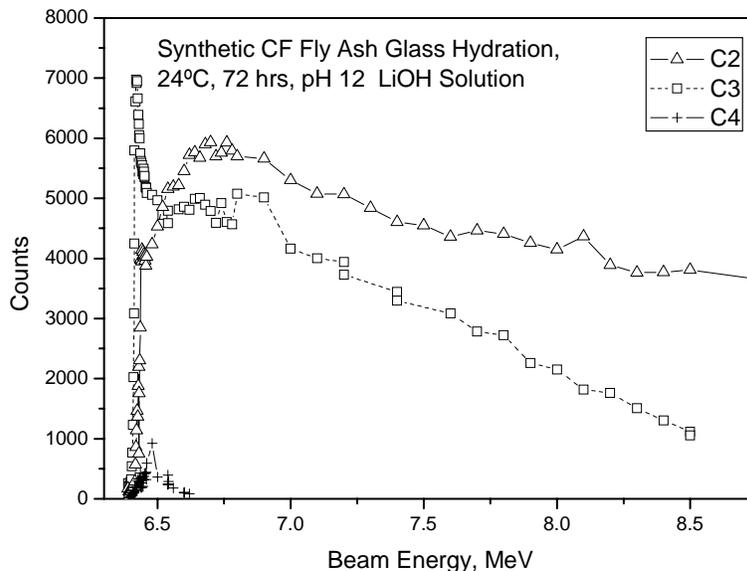


Fig. 4 NRRA hydration depth profiles in Class C type glasses

1.3 VHT: The VHT test was performed on synthetic fly ash according to the standard procedure. At 24 days, the glass sample was removed from the vessel and sliced into sections with a diamond-impregnated saw. A typical cross section of the glass is shown in Fig.5. The crystalline phases were identified as calcite and tobermorite. The gel layer thickness was determined by performing at least ten measurements across the sectioned specimen of about 40 microns thick. Since the normal diameter of a fly ash

particle is about 10-20 microns, this suggests the entire particle would be transformed into gel under these experimental conditions. The gel layer composition is close to the original glass except that the calcium content is low suggesting that the Ca is leaching out by ion exchange.

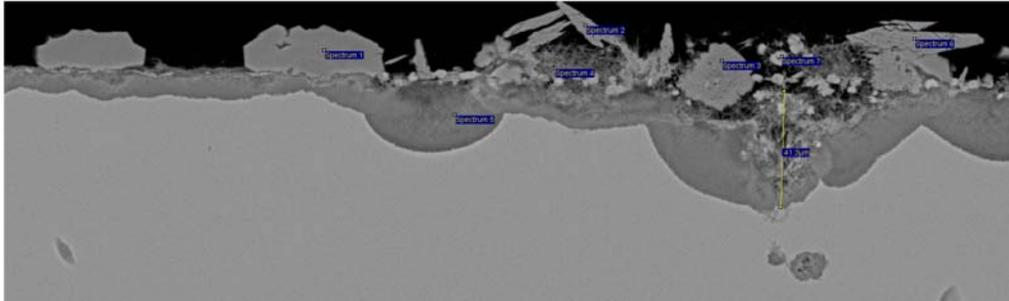


Fig. 5: SEM micrograph showing the cross section of VHT glass surface

2. Fractionated Fly Ash

A typical Class C and a Class F fly ash were separated into fractions of effective density by sink –float centrifugation. Since glass density is a function of glass composition, this provided samples of different glasses. The glasses were hydrated in pastes made with Portland cement.

2.1 Inelastic Neutron Scattering: The measurements were made at the Filter Analyzer Neutron Spectrometer (FANS) at the Center for Neutron Research at the National Institute of Standards and Technology in Gaithersburg, MD, which has a resolution on the order of 1 meV. Figure 6 shows inelastic scattering spectra from 28.08-85 meV of hydrated cement pastes incorporating Class C fly ash (a) and Class F fly ash (b) at 4 months old. The peak at energy of about 41 meV corresponds to the OH lattice mode. The large and broad peaks at higher energy levels (50 to 80 meV) can be assigned to hydrogen modes in C-S-H and water. Their peaks sit on the shoulder of this large broad band. This is removed by baseline subtraction and so the region from 35 to 45 meV has been deconvoluted and Gaussian peaks have been fitted. The results are the total amount of calcium hydroxide in the samples. The calcium hydroxide consumption is calculated from the difference between the initial amount and measured amount at specific age.

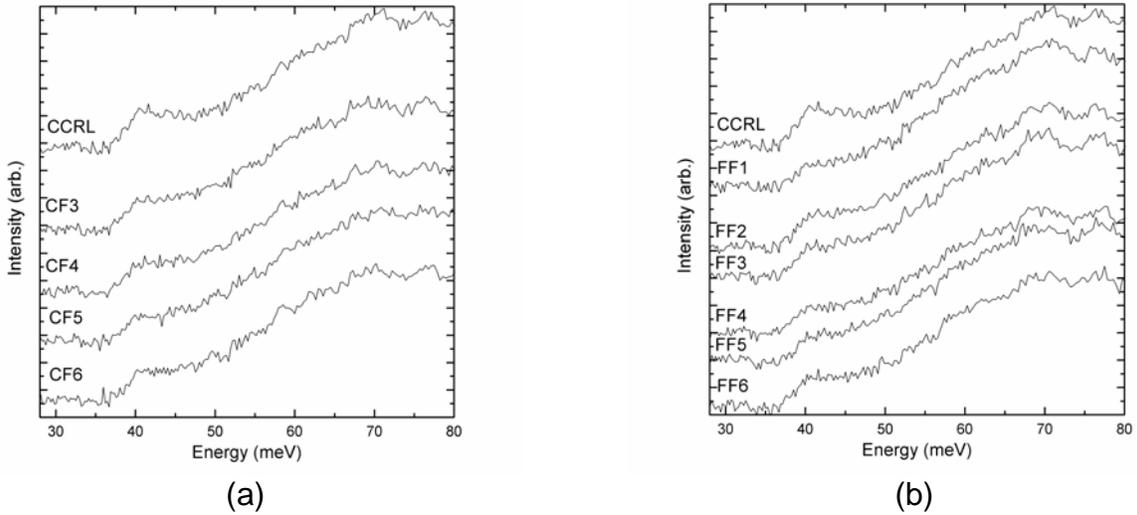


Fig. 6 Inelastic neutron scattering spectra for Type C (a) and F (b) fractionated fly Ash cement paste

2.2 Small Angle Neutron Scattering: The SANS measurements were also conducted at the Center for Neutron Research at NIST. This analytical method produces several parameters. Figure 7 shows the plot of fractal ratio and the mean diameter of different fly ash fractions which has similar composition. The result shows that, at later age of the paste, the fly ash with smaller mean diameter has higher fractal ratio or high volume fractal and less surface fractal than the fly ash with large mean diameter.

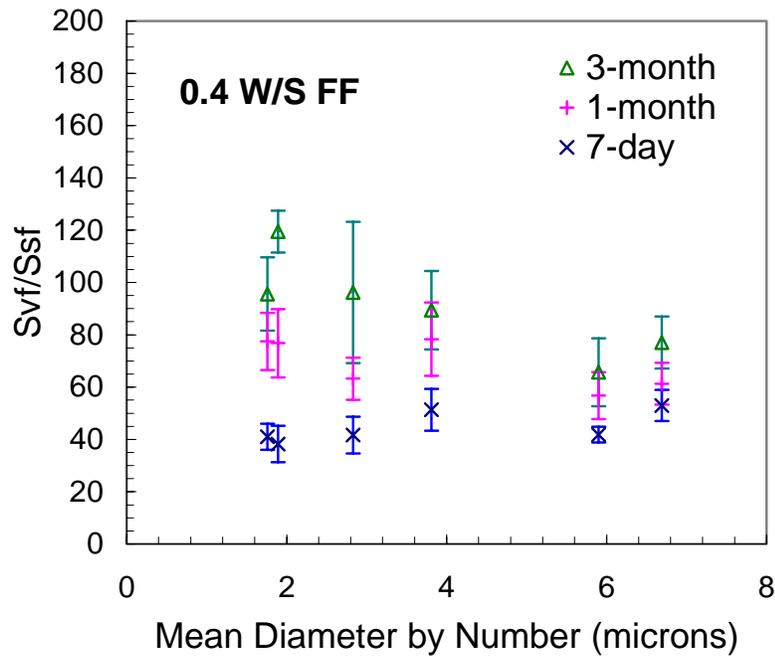


Fig.7 Fractal Ratio of FF Series vs Mean Diameter (by number)

VI. SPECIFICATION OF THE REACTIVITY VARIABLE

Finally, it is necessary to reduce the reactivity test data into a form that is suitable for use in proportioning cement/fly ash mix designs. Much recent research has concerned the development of mathematical models to describe the kinetics of the pozzolanic reaction^{41;42;43}. This produces parameters such as kinetic rate constants and reaction orders. Given the heterogeneous nature of fly ash reactions, it is also necessary to take into account physico-chemical processes which introduce the need for mass transfer coefficients and diffusion constants²⁹. This is a typical kind of problem for chemical engineering modeling. A complete solution may require independent measurement of the inert fraction and the particle size distribution of the fly ash.

An alternative approach defines the pozzolanic reactivity as Portland cement equivalents based on engineering properties defined equivalents in terms of the results of maturity or gas permeability tests⁴⁴. Bijen and van Selst (1993) described equivalence factors in terms of compressive strength, which is now the practice in several European countries⁴⁵. These equivalences are thus purely empirical and do not take advantage of knowledge of the fundamentals of fly ash reactivity.

Livingston and Bumrongjaroen (2005) have proposed a chemographic approach to proportioning fly ash/cement mixes⁴⁶. This is based on the Lever rule applied to the vector length of the line joining the cement and fly ash compositions in a suitable phase diagram. The reactivity of the fly ash is treated as an adjustment to the length of the lever arm. This can use the results of either direct or indirect reactivity tests. It can also be extended to ternary or higher order mixes and a compositional phase space of arbitrary dimensions.

VII CONCLUSIONS

For the most effective proportioning of concrete using fly ash, it is necessary to have some reliable measure of the reactivity of the specific fly ash under consideration. The reaction rate of fly ash in cement is dominated by different mechanism as the reaction progresses. These mechanisms in turn are influenced by the composition of the fly ash. Therefore it is important to understand these interactions in order to predict reactivity. Indirect tests based on measurement engineering properties of mortar or concrete may be not useful for understanding these mechanisms because of the additional factors of aggregate properties.

Direct reactivity tests involve a combination of measurand, analytical method and hydration procedure. Each combination has advantages and disadvantages, and not all combinations have been evaluated yet. Since gel formation is a common result of fly ash reactions in pH range found in concrete, it is important to have tests that can quantify this.

Certain analytical methods like SANS or NRRA can only be done at specialized facilities. However, they can serve as reference methods to calibrate and to characterize the fundamental processes controlling reactivity in order to refine other tests. Some preliminary experiments with various methods on synthetic fly ash glass indicate that chemical composition of the fly ash has a significant effect on reactivity, along with inert fraction and particle size distribution.

Finally, to be useful in proportioning cement/fly ash mixes, the results of the reactivity tests must be expressed in variables that are relevant to the mix design. This may require chemical engineering models of the physic-chemical processes involved.

Reactivity tests can have other applications beside fly ash. Ideally, it could be used for any pozzolanic material. It could also be used to evaluate alkali silica reactivity.

VIII ACKNOWLEDGEMENTS

This work was supported by US Department of Transportation to Vitreous State Laboratory. The NRRA was performed at the Ruhr-Universität Bochum by Dr. Hans-Werner Becker and Prof. Claus Rolfs with the assistance of Paloma Garcia de Viedma and Javier Sanchez of the Instituto Eduardo Torroja, Madrid, Spain and Timothy Spillane of the University of Connecticut. The SANS and IENS were performed in collaboration with Dr. Andrew J. Allen and Dr. Dan Neumann at Center for Neutron Research, National Institute of Standard and Technology.

IX REFERENCES

- [1] ASTM C311-06, Standard Methods of Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete, 04.02, 2006, American Society for Testing and Materials
- [2] O. E. Manz, Fuel, 1999, 78, pp. 133-136.
- [3] ASTM C593-06, Standard Specification for Fly Ash and Other Pozzolans for Use With Lime for Soil Stabilization, 04.02, 2006, American Society for Testing and Materials
- [4] P. K. Mehta, P.J. Monteiro, Concrete: Microstructure, Properties, and Materials, McGraw-Hill, New York, 2006,
- [5] P. K. Mehta. Process for preparation of siliceous ashes. Belgium.1973, Belgium.
- [6] D. J. Cook. Rice husk ash, In: Concrete technology and design, cement replacement materials, (Eds. R. N. Swamy), Surrey University Press, London, 1986, pp. 171-196.
- [7] P. K. Abraitis, B. P. Mcgrail, D. P. Trivedi, F. R. Livens and D. J. Vaughan, Journal of Nuclear Materials, 2000, 280, pp. 196-205.

- [8] I. S. Muller, S. Ribet, I.L. Pegg, S. Gin, P. Frugier. Characterization of alteration phases on HLW glasses after 15 years of PCT leaching, In: Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries XI, (Eds. C. C. Herman, S. Marra, D.R. Spearing, L. Vance, J.D. Vienna), Wiley, New York, 2005,
- [9] S. A. Greenburg, Journal of Physics and Chemistry, 1961, 65, pp. 12-16.
- [10] M. P. Luxan, F. Madruga, J. Saavedra, Cement and concrete research, 1989, 19, pp. 63-68.
- [11] J. Paya, M.V. Borrchero, J. Monzon, E. Peris-Mora, F. Amahjour, Cement and concrete research, 2001a, 31, pp. 41-49.
- [12] S. Sugita, M. Shoya, H. Tokuda, Evaluation of pozzolanic activity of rice husk ash, In: CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Istanbul, Turkey, 1992, pp. 495-512.
- [13] C. Tashiro, K. Ikeda, Y. Inoue, Cement and concrete research, 1994, 24, pp. 1133-1139.
- [14] E. Villar-Cocina, E. Valencia-Morales, R. Gonzalez-Rodriguez, J. Hernandez-Ruiz, Cement and concrete research, 2003, 33, pp. 517-524.
- [15] M. Frias, M.I Sanchez De Rojas, J. Cabrera, Cement and concrete research, 2000, 30, pp. 209-216.
- [16] D. J. Hassett, K.E. Eylands, Fuel, 1997, 76, pp. 807-809.
- [17] M. I. Sanchez De Rojas, J. Rivera, M. Frias, Cement and concrete research, 1999, 29, pp. 945-949.
- [18] Z. Giergiczny, Journal of Thermal Analysis and Calorimetry, 2004, 76, pp. 1572-8943.
- [19] F. P. Glasser, Calcium hydroxide in concrete, The american ceramic society, Westerville, Ohio, 2001,
- [20] R. Helmuth. Fly Ash in Cement and Concrete, In: Fly Ash in Cement and Concrete, Portland Cement Association, Skokie, Illinois, 1987,
- [21] M. B. Kruger, Q. Williams, R. Jeanloz, Journal of Chemical Physics, 1998, 91, pp. 5910-5915.
- [22] R. A. Livingston, J. S. Schweitzer, C. Rolfs, H.-W. Becker and S. Kubsy, Journal of material research, 2000, 16, pp. 687-693.

- [23] R. A. Livingston, W. Bumrongjaroen. Inelastic Neutron Scattering Measurement of Pozzolan Performance in Portland Cement, In: *Nondestructive Characterization of Material XI*, (Eds. R. B. Green, B.B. Djordjevic, and M.P. Hentschel), Springer, Berlin, Germany, 2003, pp. 615-620.
- [24] J. S. Schweitzer, R. A. Livingston, et al., In Situ Measurements of the Cement Hydration Profile during the Induction Period, In: *12th International Congress on the Chemistry of Cement*, Montreal, Canada, 2007, pp. in review.
- [25] A. J. Allen, R.A. Livingston, *Advanced cement based materials*, 1998, 8, pp. 118-131.
- [26] A. J. Allen and R. A. Livingston. Small-angle Scattering Study of Concrete Microstructure as a Function of Silica Fume, Fly Ash or Other Pozzolanic Additions, In: *Fifth Canmet/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, (Eds. V. Malhotra), American Concrete Institute, Detroit, 1995, pp. 1179-1200.
- [27] J. W. Schmitt, D.C. Stark. Recent progress in the development of the osmotic pressure to determine potential for alkali silica reactivity of aggregates, In: *Proceedings of the eighth international conference on alkali aggregate reaction*, Kyoto, Japan, 1989,
- [28] D. Stark. Osmotic test cell to identify potential for alkali-aggregate reactivity, In: *6th International conference on alkalis in concrete*, Copenhagen, Denmark, 1983,
- [29] E. V.-M. Villar-Cocina E., R. Gonzalez-Rodriguez, J. Hernandez-Ruiz, *Cement and concrete research*, 2003, 33, pp. 517-524.
- [30] S. A. Fitzgerald, D.A. Neumann, Et.Al. , *Journal of Materials research*, 1999, 14, pp. 1160.
- [31] N. Nemes, D.A. Neumann, Et.Al., *Journal of Materials research*, 2006 21, pp. 2516-2523.
- [32] A. J. Allen, C.G. Windsor, V.S. Rainey, D. Pearson, D.D. Double, N.McNalford, *Journal of Physics D*, 1982, 15, pp. 1817-1833.
- [33] J. J. Thomas, H.M Jennings, A.J. Allen, *Cement and concrete research*, 1998, 28, pp. 897-905.
- [34] G. J. Verbeck, C. Gramlich, *ASTM Proceedings*, 1955, 55, pp. 1110-1128.
- [35] C. M. Jantzen, N.E. Bibler, D.C. Beam, W.G. Ramsey, and B.J. Waters. Nuclear waste glass product consistency test (PCT) version 5.0 (U).1992, Westinghouse Savannah River Company. 125.

- [36] WK84: New Test Method for Measuring Waste Glass Durability by Vapor Hydration Test, C26.13, 2006,
- [37] W. Bumrongjaroen and R. A. Livingston, Synthetic Glass Models for Investigating Fly Ash Reactivity, In: 9th CANMET/ACI International Conference on Fly Ash in Concrete Warsaw, Poland, 2007, pp. accepted.
- [38] W. Bumrongjaroen, S. Swatekititham, R. A. Livingston, M. Manghnani and J. S. Schweitzer. Calcium Aluminate Silicate Glass as a Model System for Investigating Fly Ash Reactivity. PacRim 6.2005, Maui, HI, American Ceramic Society.
- [39] J. Aichison, Statistical Analysis of Compositional Data, Wiley, New York, 1983,
- [40] S. Swetakititham. Effect of Chemical Composition on the Dissolution Rate of Synthesized Fly Ash. NRC-EHWM.2005, Bangkok, Chulalongkorn University.
- [41] P. R. Khangaonkar, A.Rahmat, K.G. Jolly, Cement and concrete research, 1992, 22, pp. 577-588.
- [42] M. Frias, J. Cabrera, Cement and concrete research, 2002, 32, pp. 133-139.
- [43] W. Jander, Z. Anorg. Allg. Chem. , 1927, 163, pp. 1-30.
- [44] R. H. Mills. Evaluation of fly ash on the basis of mass equivalent maturity equivalent and permeance, In: Fly ash and coal conversion by-products: characterization, utilization and disposal II, (Eds. G. J. McCarthy, F.P. Glasser, and D.M. Roy), 1986, pp. 255-262.
- [45] J. Bijen, R. Van Selst, Cement and concrete research, 1993, 23, pp. 1029-1039.
- [46] R. A. Livingston, and Bumrongjaroen, W., Optimization of Silica Fume, Fly Ash and Cement Mixes for High Performance Concrete, In: World of Coal Ash Lexington, KY, 2004, pp.