Fly Ash Reactivity as a Glass Corrosion Topic

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Abstract

In order to achieve the goal of ultra high performance concrete, which involves the addition of fly ash, a better understanding is needed of the fundamental properties and reactivity of the glassy phase in fly ash. The theory of the chemical durability of glass can provide a fundamental understanding in terms of the influence of chemical composition on the polymerization and aluminum saturation of the fly ash glass. This can serve as the basis for a more rigorous classification system for fly ashes. Glass science also provides a number of analytical methods that can be adapted for characterizing fly ash and for determining its reactivity. The use of synthetic glass samples with appropriate compositions as standard specimens it possible to intercompare data from different reactivity tests. It also makes it feasible to apply advanced techniques such as neutron scattering and NRRA to yield insights into the fundamental processes controlling the reaction kinetics.

1. Introduction

Fly ash is extensively used in concrete industry as it provides more strength and durability to concrete matrix through its pozzolanic activity. The reactivity of fly ash depends mainly on its glassy content; the kinetics of the fly ash reaction thus depends upon the leaching rate of these ions from its glass fraction. To maximize the rate of the reaction it is desirable to have as high a leach rate as possible. This is the opposite of the usual situation involving water/glass interactions, in which the objective is to minimize the leach rate for greater durability.

The subject of glass durability or corrosion is of interest in a number of fields of glass science including nuclear waste management[1], art conservation[2], commercial glass manufacture[3] and geochemistry of rock weathering[4]. Nevertheless, the theory and experimental methods of glass science should still be applicable to fly ash glass. Therefore, this paper presents an overview of fly ash reactivity in terms of the glass science approaches to chemical composition phase diagrams, materials characterization, and reactivity tests and models.

Glasses are amorphous materials that occur when certain liquids are cooled below their melting points at a rate faster than they can grow crystal structures[5]. In the specific case of fly ash glass particles, these are formed by fusion of clay particle inclusions in the coal during the combustion process [6]. As the combustion products pass out of the flame, the droplets of the melt cool rapidly into glassy spheres that are predominantly calcium aluminosilicate (CAS) glass.

2. Calcium Aluminate Silicate Glass Science

A variety of inorganic and organic materials can form glassy networks, but the network former of main interest here is silica (SiO_2). The melting temperature of pure silica is about 1,700°C. However, most practical applications of silicate involve the addition of other elements that act as fluxes to lower the melting temperature to a range of 1100 -1400 °C. Typically these additions are the alkalis sodium and potassium or the alkaline earths, calcium and magnesium. In glass science terminology, these groups as network modifiers[3]. In addition to silica Al_2O_3 is regarded as a network former, although, as described below, alumina can actually play several roles; and Fe_2O_3 acts as either intermediate or modifier

For example, the conventional phase diagram showing the relationship of fly ash compositions to other pozzolanic materials uses the triaxial plot CaO Al_2O_3-SiO_2 [7]. As an alternative, following an approach used in glass conservation[2], the major oxides can be grouped by their potential glass network functions into a three component system: Al_2O_3-SiO_2-Fe_2O_3, CaO, and Na_2O-K_2O as shown in the triaxial diagram in Fig. 1. Data acquired by a Computer Controlled Scanning Electron Microscope (CCSEM) analysis of individual fly ash particles are plotted in the diagram[8]. For comparison the boundaries defined by ASTM C-618 for Class C and Class F are also shown. It can be seen that the fly composition varies significantly in both alkali and alkaline earths, but the
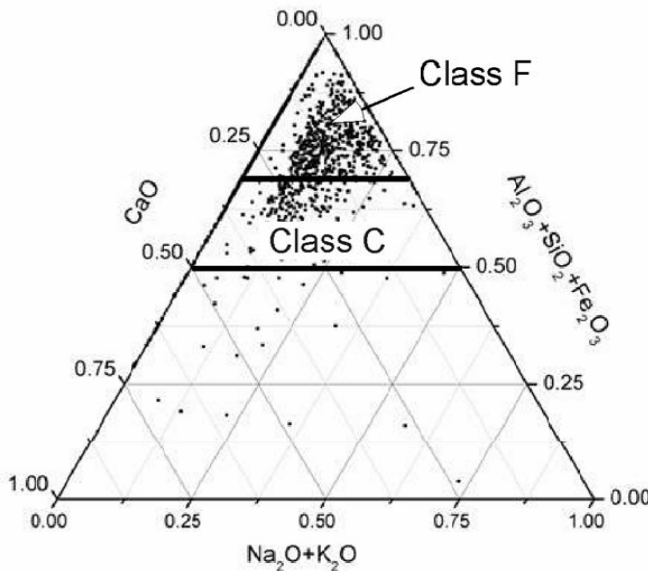

Figure 1: Compositions of individual Class C fly ash glass particles in glass

ASTM C-618 classifications are insensitive to these variations. These are important for glass durability because they affect the polymerization of the silicate ions.

The silicate ion, $SiO_4{-}^4$ consists of a silicon atom at the center of a tetrahedron formed by four oxygens. In pure silica glass the tetrahedral are all connected to each other by bridging oxygen bonds to form a disordered network. These bonds are very strong, and hence the glass is relatively unreactive. However, if other elements are introduced the bonds are broken, and the glass typically becomes more reactive. This effect is quantified in terms of the non-bridging oxygens per silicate tetrahedron or NBO/T [9]. This index can range from 0 to 4, and it can take on non-integer values, reflecting the fact that the silicate ions can form clusters of various sizes and morphologies [3]. The NBO/T is thus a measure of the polymerization of the silicate ions. A low value for NBO/T indicates a high degree of polymerization and vice versa.

The degree of polymerization can be determined experimentally using Nuclear Magnetic Resonance (NMR)[10] or Raman spectroscopy. The latter is an optical spectroscopy method based on the inelastic scattering of light. It is sensitive to the chemical environment around atoms, and thus it can be used to analyze the polymerization of silicate ions in a CAS glass[11]. It has been applied previously to characterize the glass content in actual fly ashes[12]. The number of bridging oxygens per silicate tetrahedron is expressed as its Q number. Q^4 indicates 4 bridging oxygens, Q^o indicates no bridging oxygens etc.
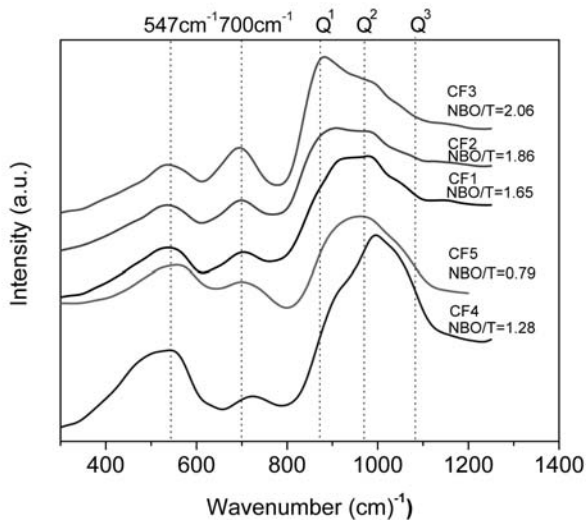

Figure 2: Raman spectra for Class C type synthetic fly ash glasses

The Raman spectra for a Class C-type series are plotted in Fig. 2 These were obtained from synthetic fly ash specimens described below. The bands observed in 800-1200 cm^{-1} region show the effects of calcium ions and aluminum ion on the Si-O bonds. The broken lines indicate the position of species Q^1 at 880 cm^{-1}, Q^2 at 960 cm^{-1}, and Q^3 at 1085 cm^{-1} [13]. The NBO/T for each glass is also given. This shows that the NBO/T increases with greater Q^1 content, i.e. with lower polymerization.

X-ray diffraction, although typically used to charac-terize ordered crystal structures can also provide information on disordered materials. The diffraction pattern of silicate glasses, while lacking sharp Bragg peaks, typically has a broad hump or halo centered on the principal line of cristobalite (I_o=4.05) indicating the loss of long range order. It has been reported by Diamond that the value of the halo's maximum, 2θ max, correlates with the chemical CaO content of the glass [14]. They proposed that a low angle halo represents a highly polymerized SiO_2 network, while higher angle halo the decreasing polymerization. However, as discussed below, Ca can affect reactivity in several ways depending on other components present.

The presence of Al_2O_3 in CAS glasses creates complications because the aluminum atom can also go into tetrahedral coordination. However, since it has only a 3+ charge compared to the 4+ of Si, the charge has to be balanced by the alkalis and alkaline earths. This condition is expressed by the aluminum saturation index, ASI =Al/(Na + K + 2Ca). Glass compositions with ASI >1 are called peraluminous. In this range, the aluminum can act as both a network former and a network modifier. In this case the NBO/T calculation includes both Si and Al tetrahedra. Hubbard et al found for a specific set of United Kingdom fly ashes that the the reactivity increased with the K/Al ratio [15]. This suggests that the ASI could be a useful predictor of reactivity.

Those glasses with ASI<1 are subdivided into 2 categories: peralkaline for Na + K > 2Ca and calcium-rich for Na + K < 2 Ca. Calcium is usually present in fly ash glass in higher concentrations than the alkalis and also varies over a greater range. As such, it is the major element that controls the durability of glass in fly ash. In peralkaline, or typical Class C fly ash, calcium would act as a network modifier. Thus the greater the calcium content, the higher the NBO or the lower the durability. In peraluminous glass, the calcium would act as a charge balancer, and the Al content would be more important than the calcium in controlling the durability of glass. Therefore, the calcium content can have divergent effects on the glass durability depending on the glass composition.

A related property of the glass, its optical basicity, can be calculated from the density and the refractive index [16]. This is a measure of the glass's role as a Lewis acid or base[17]. It is thus a possible indicator of chemical reactivity[18]. The optical basicity can also be measured experimentally by the frequency shifts in the ultra-violet spectra of probe ions such as Pb^{2+}.

3 Glass Corrosion Models

Models to predict glass durability or corrosion have been based on either theory or empirical measurement. The theoretical models usually take a thermodynamic approach and essentially estimate the chemical affinity or departure for equilibrium. The empirical models predict leach or etching rates in terms of chemical kinetics.

Theoretical models compute an index from the chemical composition that predicts relative resistance to water. Adams has proposed the NBO/T itself as such an index[19]. The sum Al_2O_3+ SiO_2 + Fe_2O used in ASTM C-618 can be viewed as a crude type of compositional index, but as noted above, it is not relevant to CAS glass reactivity. A two-dimensional classification based on the NBO/T and the ASI may be more useful. However, none of these indices take into account the variations in free energy which is the driving force in the reaction.

Linear Free Energy models are based on the linear combinations of the hydration free energies of the individual constituents[20]. They have been somewhat successful in predicting the reactivity of different types of glasses over several orders of magnitude [19]. However, these have been criticized on the grounds that they do not take into account the interactions between the constituents [20]. In order to account for these interactions, some type of activity coefficients similar to those used in electrolyte solutions should be developed. One such activity based model is the structural bond strength (SBS) model [21]. It is a linear free energy model in which the enthalpy of hydration is modified by the estimated bond strengths of the constituents as determined from a set of empirical rules proposed by Sun[22] based on network formers, modifiers and breakers.
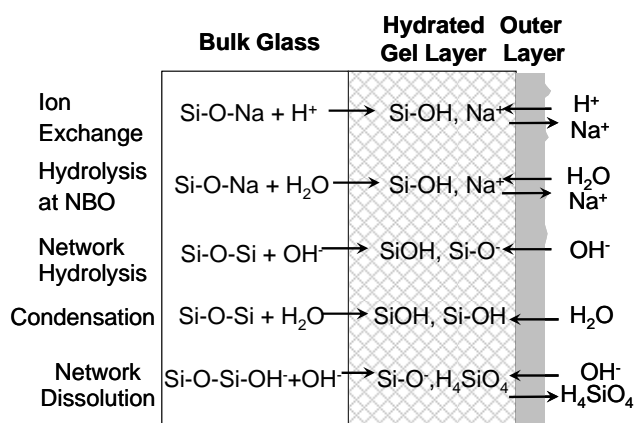

Figure 3: Schematic diagram of glass hydration surface layers

A well-known issue with thermodynamics in general is that they may not accurately predict the actual kinetics of a given reaction. This is a particular problem with glass corrosion which is a heterogeneous reaction involving several ionic species. The kinetics thus include a number of possible rate limiting steps: diffusion within the glass, ion exchange, and hydrolysis [3]. The water dif-fuses into the glass matrix, where it

undergoes ion exchange processes to break down the glass network and lead to glass dissolution. The high pH in pore solutions of concrete mixes significantly increases the solubility of silica species, thereby increasing the rate of dissolution. However, this also promotes the formation of gels at the glass surface that can inhibit ion transport into solution. A typical structure of surface layers resulting from the interaction of these kinetic processes is presented schematically in Fig 3.

4. Glass Reactivity Measurements

A variety of tests for pozzolanic reactivity have been proposed by a number of researchers[23]. These are summarized in Table I. This includes standard tests developed for nuclear waste glass corrosion along with others developed specifically for fly ashes or alkali-silica reaction. There is not sufficient space here to describe them in detail. In general, the leaching tests have been intended for low to neutral pH conditions typically found in nature. However, as discussed above, in conditions found in concrete the ions may be trapped in gels on the glass surface. Thus it is necessary to consider other approaches that quantify the amount of gel formed or the depth of leaching. Some of these such as small angle (SANS) and inelastic neutron scattering (IES) 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 laboratory

Table I: Reactivity tests

MEASURAND	ANALYSIS	REFERENCES
Ion leaching	Wet chemistry (PCT, SPFT, TCLP)	[1, 24]
CH consumption	Calorimetry, XRD, IENS	[25, 26]
Hydration layer depth	NRRA, VHT	[27] [28]
Gel surface area	SANS	[29]
Gel volume	Osmotic pressure	[30, 31]
Surface etch depth	RBS, profilometry, VHT	[3, 28]

5. Synthetic Fly Ash Glass Preparation and Analysis

In order to investigate the fly ash glass approach to fly ash reactivity , it is necessary to have a representative range of glass compositions. However, it is difficult to accomplish this with actual fly ash samples because of limited compositional ranges, varying inert fractions and particle size effects. Thus, the approach chosen here is to make to use of glassmaking techniques to produce specimens with compositions similar to those of fly ash in order to serve as model systems[32, 33].

Two series of CAS glasses were prepared from mixtures of the oxides SiO_2, Fe_2O_3, Al_2O_3, N_2O, CaO, MgO, and K_2O [34]. After the glass speci-mens were prepared, several analytical techniques were applied to characterize their macroscopic properties.   These included X-ray diffraction for crystallinity, refractive index, density, elemental analysis, particle size distribution, and Raman spectroscopy for silicate speciation.

Some of the results using these glasses in the Single Pass Flowthrough (SPFT) test are shown Figs.4a and 4b. This is a leach test that involves a flowing solution instead of a batch or static test in order to maintain constant undersaturated conditions and the desired pH [24].   The synthetic fly ashes were immersed in a strong LiOH 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[35]. Figures 4a and 4b show the normalized cumulative mass losses of elements over time of two Class C-type glasses. The results showed an order of magnitude difference between the two samples, again indicating that the ASTM C-618 index do es not adequately describe reactivity.   Note that the Si dissolution mechanism proceeds simultaneously with the Na, K interdiffusion
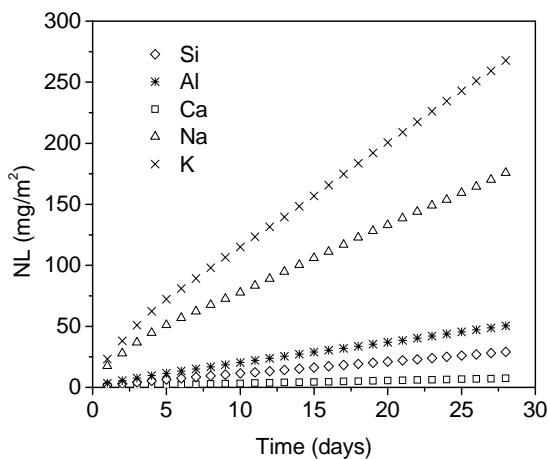
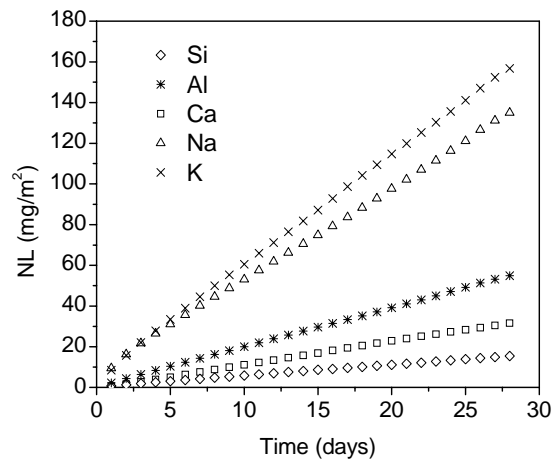Figure 4a: Cumulative mass loss for CF2 in pH 12.5 solution

Figure 4b: Cumulative mass loss for CF3 in pH 12.5 solution

mechanism and becomes dominant at later ages. The leaching rates of ions in both Type C and Type F glasses are in the descending order of K>Na>Al>Si>Ca>Mg>Fe. The dissolution rate of Si depends on the concentrations of Na and K in these glasses. It is also found that glass with a high ASI yields a low dissolution rate of Si because the alumina buffers both the mono-and divalent cations.
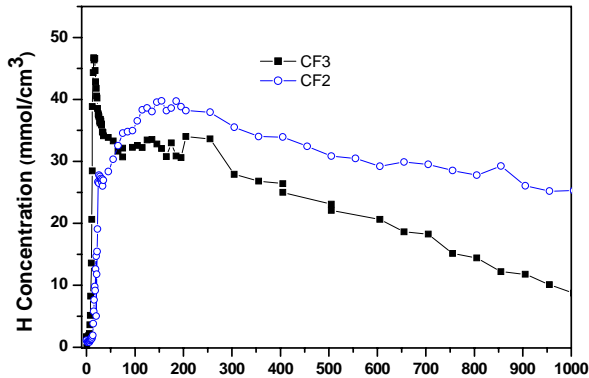

Figure 5. NRRA hydration depth profiles in Class C type glasses

The nuclear resonance reaction analysis (NRRA) method is an ion beam technique that uses the resonance capture of ^{15}N ions by hydrogen to measure the depth profile of hydration, This tech- nique is described in detail in another paper in these proceedings[36]. Examples of NRRA hydration depth profiles are shown in Fig. 5 for the glasses CF2 and CF3. Since all the specimens were hydrated for the same amount of time, the area under each curve gives a crude measure of the relative reactivity. At depth, the amount of hydrogen is greater for CF2, which is consistent with the greater amount of leaching observed in the SPFT curves. However, at the surface the concentrations of hydrogen are reversed and there is a 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. This may be another reason for the lower concentrations of ions observed in solution for this sample (Fig. 4b). In contrast, for CF2 there is no surface layer and instead the curvature of the profile suggests a much more open structure. Further electron microscope analyses of leached glass surfaces are underway.

6. Conclusions

The development of performance-based standards for fly ash requires an improved understanding of reactivity of the material. The theory of the chemical durability of glass can provide a fundamental understanding in terms of the influence chemical composition on the polymerization and aluminum saturation of the fly ash glass. This can serve as the basis for a more rigorous classification system for fly ashes.   Glass science also provides a number of analytical methods that can be adapted for characterizing fly ash and for determining its reactivity.

However, much of the existing literature concerns measurements made in solutions of low to neutral pH. At the pH levels found in concrete, the glass tends to develop surface layers and precipitate colloids and gels. Therefore, it is necessary to conduct systematic studies of the effect of glass composition on reactivity under these conditions. It is difficult to study this in real fly ashes because of the heterogeneity in chemical composition and mineralogy from one particle to another. It is not practical to isolate particles of specific glass compositions from raw fly ash. An alternative approach is to prepare synthetic glass samples with appropriate compositions as standard specimens. This makes it possible to intercompare data from different reactivity tests. It also makes it feasible to apply advanced techniques such neutron scattering and NRRA to yield insights into the fundamental processes controlling the reaction kinetics. Preliminary results have shown agreement with glass durability theory and demonstrated the advantages of using a synthetic glass model for fly ashes.

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