

Influence of a fine glass powder on cement hydration: Comparison to fly ash and modeling the degree of hydration

Nathan Schwarz, Narayanan Neithalath *

Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699, USA

Received 2 June 2007; accepted 4 December 2007

Abstract

This paper reports the results of an investigation carried out to understand the influence of a fine glass powder on cement hydration. The pozzolanicity of the glass powder and a Class F fly ash for comparison was evaluated using strength activity index over a period of time, and a rapid electrical conductivity based method. Flame emission spectroscopy and electrical conductivity tests were used to quantify the alkali release from glass powder, and gain information on the rate of alkali release. It was found that the glass powder releases only a very small fraction of sodium ions into the solution. It was observed that the glass powder modified pastes show higher non-evaporable water contents than the plain paste and fly ash modified pastes, indicating that glass powder facilitates enhancement in cement hydration. An expression has been developed for the change in non-evaporable water content as a result of enhancement in cement hydration and the hydration of the cement replacement material. The efficiency of any cement replacement material with age in the paste system can be quantified using this parameter. Based on this parameter, a 5% cement replacement with glass powder was found to be effective at the chosen water-to-cementing materials ratio (w/cm), whereas at higher replacement levels, the dilution effect dominates. A model to predict the combined degree of hydration of cement pastes incorporating more than one cementing material is outlined. The measured and predicted combined degrees of hydration agree well.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Glass powder; Fly ash (D); Cement paste (D); Alkalies (D); Hydration (A); Degree of hydration (B); Non-evaporable water content

1. Introduction

Supplementary cementing materials (SCM) have become an integral part of Portland cement concrete. They are useful in improving the mechanical and durability properties of concrete by beneficially impacting the material microstructure. The properties of common SCMs like fly ash and silica fume, and performance of concrete incorporating such materials are well documented. A variety of other waste or recycled materials with supplementary cementing potential are available, and their use in concrete becomes an increasingly attractive option if there are environmental issues related to their disposal. Fine glass powder is one such material, which is the focus of this paper. Glass contributes a

major share of the total solid waste that is disposed every year. The recycling of waste glass is a major issue in urban areas of developed countries [1,2], which has resulted in significant interest of late in utilizing it in concrete.

Crushed glass has been used as a coarse aggregate in concrete [3–6]. Attempts were made to use waste glass as a raw siliceous material in the production of Portland cement [7,8]. The use of coarse glass powder as a hydration enhancing filler has been explored [9,10]. However, value addition of glass in concrete is best achieved if it is used as a cement replacement material. Glass is amorphous and has high silica content, which are the primary requirements for a pozzolanic material. A particle size of 75 μm or less is reported to be favorable for pozzolanic reaction [11]. The high alkali content of glass is a typical concern for its use in concrete, but studies [1,2] have shown that finely ground glass does not contribute to alkali–silica reaction.

A few studies have investigated the potential of finely ground waste glass powder as a pozzolanic material [2,11–14].

* Corresponding author. Department of Civil and Environmental Engineering, Box 5710, Clarkson University, Potsdam, NY 13699, USA. Tel.: +315 268 1261; fax: +315 268 7985.

E-mail address: nneithal@clarkson.edu (N. Neithalath).

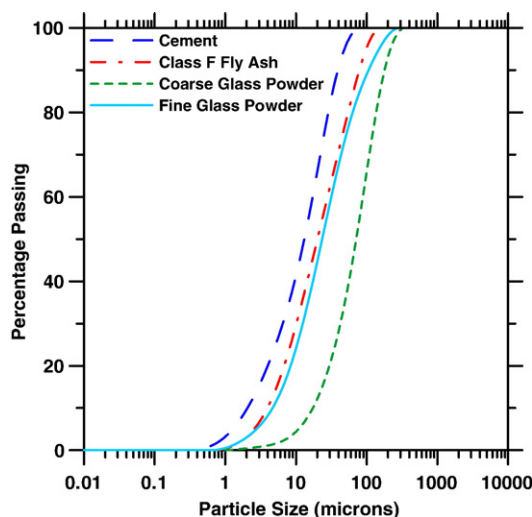


Fig. 1. Particle size distribution of cement, glass powders, and fly ash used in this study.

These studies have investigated the particle sizes, mechanical property development, and alkali–silica reactivity of mortars incorporating glass powder. This paper focuses on (i) examining the alkali release characteristics of the glass powder, (ii) influence of glass powder on cement hydration in pastes, and its comparison to fly ash, and (iii) a model to predict the total degree of hydration (both of the cement and the SCM) in pastes incorporating a SCM. Though a series of other tests to characterize the glass powder and compare it to fly ash like determination of flow value, setting times, compressive strengths, calcium hydroxide contents using thermal analysis, and heats of hydration were also carried out, they are not elaborated in this paper. Some of those results are reported in [15].

2. Experimental program

2.1. Materials and mixtures

Type I ordinary Portland cement conforming to ASTM C 150, fly ash conforming to ASTM C 618, and a fine glass powder

Table 1
Chemical composition and physical properties of cement, glass powder, and fly ash used in this study

Composition (% by mass)/ property	Cement	Fine glass powder	Fly ash
Silica (SiO ₂)	20.2	72.5	50.24
Alumina (Al ₂ O ₃)	4.7	0.4	28.78
Iron oxide (Fe ₂ O ₃)	3	0.2	5.72
Calcium oxide (CaO)	61.9	9.7	5.86
Magnesium oxide (MgO)	2.6	3.3	1.74
Sodium oxide (Na ₂ O)	0.19	13.7	0.96
Potassium oxide (K ₂ O)	0.82	0.1	—
Sulfur trioxide (SO ₃)	3.9	—	0.51
Loss on ignition	1.9	—	2.8
Fineness, % passing (sieve size)	97.4 (45 μ m)	80 (45 μ m)	80 (45 μ m)
Specific surface area (m ² /kg)	388	—	—
Density (kg/m ³)	3150	2490	2250

are used to prepare the cement pastes used in this study. The particle size distribution (PSD) of these materials, along with that of a coarse glass powder (for comparison) is shown in Fig. 1. The chemical composition and physical characteristics of the cement, fine glass powder, and fly ash used in this study can be found in Table 1. The cement pastes were prepared with a water-to-cementitious materials ratio (w/cm) of 0.42. Cement was replaced by either glass powder or fly ash at rates of 5%, 10%, and 20% by mass. Mortar specimens in which glass powder or fly ash replaced 20% of the cement were also prepared as per ASTM C 311 to determine the strength activity indices.

2.2. Test methods

The strength activity indices of the plain and modified pastes were determined in accordance with ASTM C 311. The alkali release from glass powder was qualitatively determined using electrical conductivity tests, and confirmed using flame emission spectroscopy.

The loss on ignition method was used to determine the non-evaporable water content at all selected ages of hydration. Small pieces from the samples (approximately 1–2 mm in size) cured in saturated limewater were pulverized and soaked in acetone to stop further hydration. The pulverized samples were heated in an oven at 105 °C for 24 h, followed by heating in a muffle furnace at 1050 °C for 3 h. The non-evaporable water content (w_n) was obtained as the difference in mass between the sample heated at 105 °C and 1050 °C normalized by the mass after heating to 1050 °C, and correcting for the loss on ignition of unhydrated cement (or of the unhydrated cement and the replacement material multiplied by their respective mass fractions). In addition to the pastes described above, plain and modified pastes were made with a w/cm of 0.80 and cured in saturated limewater for 140 days. The non-evaporable water content of these high w/cm pastes was determined to facilitate the calculation of degrees of hydration of the 0.42 w/cm pastes at various ages.

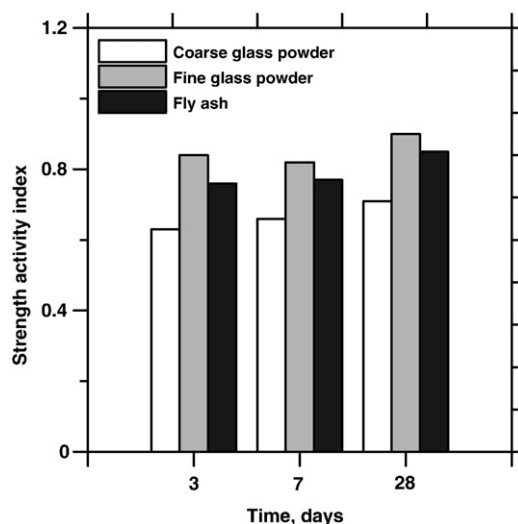


Fig. 2. Strength activity indices of glass powder and fly ash modified pastes.

3. Results, analysis, and discussion

3.1. Pozzolanicity of glass powder and fly ash

The pozzolanicity of glass powder and fly ash modified pastes was determined using the strength activity index, as per ASTM C 311, as well as a rapid procedure that uses reduction in electrical conductivity as an indicator of pozzolanic activity [16].

Fig. 2 depicts the strength activity index of coarse and fine glass powders, and fly ash at 3, 7, and 28 days. The coarse glass powder shows the lowest strength activity index, whereas the fine glass powder shows the highest strength activity index at all the chosen ages. The w/cm required to produce a flow of 110 ± 5 for the fine glass powder and fly ash mixtures was 97% of the w/cm of the plain paste. The strength activity indices show that the fine glass powder modified mixtures can develop strength at a rate similar or higher than that of the class F fly ash at the specified ages.

The pozzolanic activity of fine glass powder and fly ash was also evaluated using the variation in electrical conductivity of a saturated calcium hydroxide solution in which the SCM is mixed in [16]. 5 g of fine glass powder or fly ash was mixed into 200 ml of saturated calcium hydroxide solution maintained at 40 °C. The reduction in electrical conductivity of the solution was monitored for the first 2 min. According to [16], the replacement material can be classified as non-pozzolanic if the conductivity reduction is less than 0.04 S/m, variably (moderately) pozzolanic if the conductivity reduction is between 0.04 and 1.2 S/m, and highly pozzolanic if the conductivity reduction is greater than 0.12 S/m. The solutions containing either fine glass powder or fly ash showed a conductivity reduction of 0.10 S/m and 0.08 S/m respectively, indicating moderate pozzolanicity. A companion test using silica fume showed a conductivity reduction of 0.13 S/m, which can be interpreted as an indication of high pozzolanicity.

3.2. Alkali release from glass powder

The influence of alkalis on cement hydration is well documented. Higher alkali ion concentration in the pore solution is expected to result in an acceleration of the early hydration in cement pastes [17,18], and reduced reaction rates over time [19]. It is well understood that the alkali ions depresses the solubility of Ca^{2+} ions [17,20]. The higher early strength of cement pastes mixed with NaOH has been attributed to the increase in the formation of ettringite [17]. Since the glass powder used in this study has a high alkali content (13.7% Na_2O), information on the amount and rate of alkali release is required in order to gain satisfactory understanding of the performance of cement based materials incorporating glass powder. Flame emission spectroscopy was used to quantify the amount of sodium released from the fine glass powder and electrical conductivity was used to gain information on the rate of alkali release, and qualitatively assess the alkali levels in the solution.

3.2.1. Flame emission spectroscopy

5 g of glass powder was mixed thoroughly in 200 ml of saturated calcium hydroxide solution. The solution was filtered,

and aspirated into a flame and atomized. The absorption of light at a wavelength of 330.2 nm was measured and compared to a calibration curve that relates the energy absorbed to known sodium concentrations. A less sensitive wavelength of 330.2 nm was used instead of 589 nm because of the relatively higher concentration of sodium. The solution without glass powder was also subjected to flame emission and the difference in sodium concentrations between the samples with and without glass powder is taken as the contribution from glass powder, which for this study was 26.04 mg/l. Based on the sodium content in the glass powder, if all the sodium is released into the solution, the resultant concentration should have been 506 mg/l. This shows that the glass powder is releasing only a very small proportion of sodium into the solution.

3.2.2. Electrical conductivity

Fig. 3a shows the variation in electrical conductivity of plain and glass powder modified pastes with time, determined using the bulk resistance obtained from frequency dependent electrical

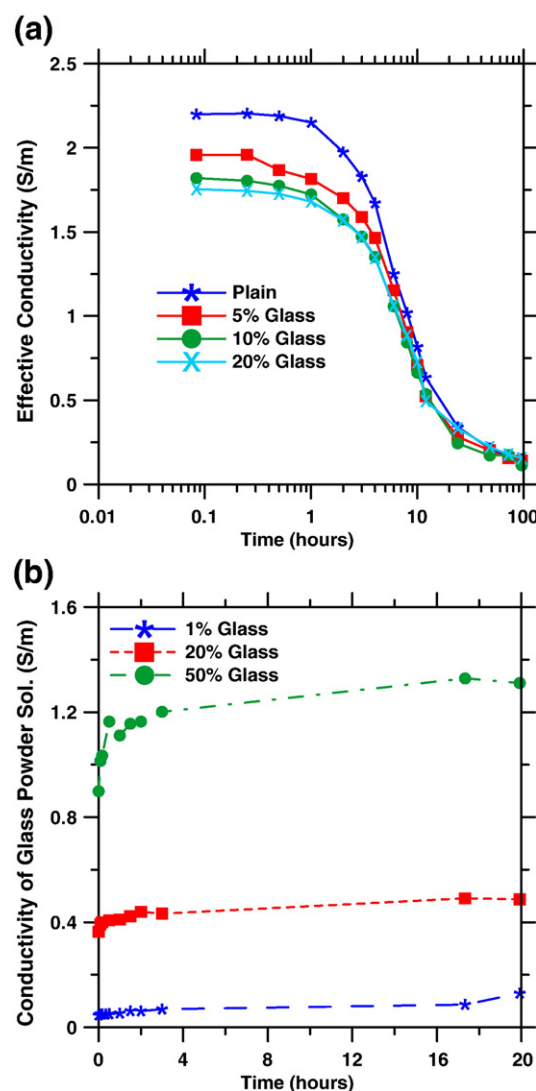


Fig. 3. Electrical conductivity as a function of time for (a) plain and glass powder modified cement pastes, (b) glass powder solutions.

impedance measurements, the procedure for which has been extensively reported [10,21–23]. At very early ages, the conductivity of the paste with the highest replacement of cement by glass powder is found to be the lowest. Since the Na^+ and K^+ ions have a large influence on the conductivity, it is evident that their reduction caused by the lower cement content is not compensated by the alkalis from glass powder.

To understand the rate of alkali release and qualitatively assess the amounts of alkalis released, glass powder was dissolved in de-ionized water at concentrations of 1, 20, and 50%. The electrical conductivities of these solutions were measured until 20 h and are plotted in Fig. 3b. A noticeable increase in conductivity occurs only in the first hour or so, indicating that the water soluble alkalis are released within that time. If all of the Na_2O of glass powder dissolves in water according to $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$, then the NaOH concentrations corresponding to the mixtures stated above are 0.044 M, 0.88 M, and 2.2 M respectively. The conductivities of NaOH solutions of these concentrations were determined to be 6.1 S/m, 29.6 S/m, and 43.4 S/m respectively, which are higher by an order of magnitude or more than the values shown in Fig. 3b.

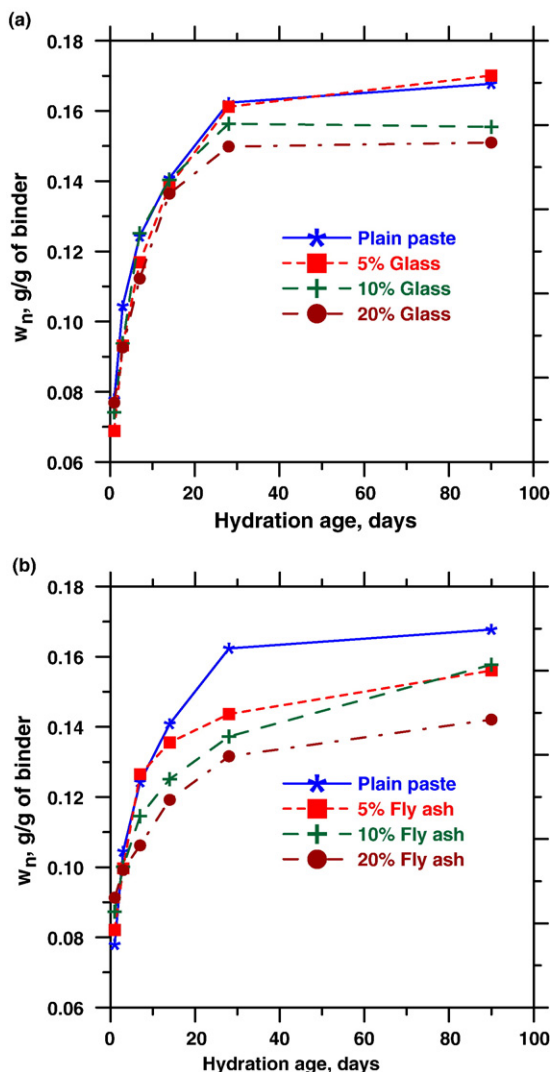


Fig. 4. Non-evaporable water content per gram of binder of (a) glass powder and (b) fly ash modified cement pastes.

This also proves that the glass powder is releasing only a very small fraction of alkalis into the solution, confirming the results from flame emission spectroscopy. The consequences of dilution effect (reduction in cement content, similar to pastes modified with fly ash) thus dominates, which results in slightly delayed setting times and reduced early age strengths for the glass powder modified pastes compared to the plain paste [15]. This also points to the fact that adding a small amount of glass powder will not be a viable means of alkali activation of other SCMs. If the alkali ions are not released into the pore solution, the risks for alkali–silica reaction are also greatly reduced.

3.3. Non-evaporable water content

Non-evaporable water contents (w_n) of cement pastes are commonly used to ascertain their degrees of hydration. Fig. 4a and b show w_n per gram of binder for glass powder and fly ash modified pastes until an age of 90 days. It is observed that most of the modified pastes, either glass powder or fly ash, have lower w_n per gram of binder compared to plain pastes. This trend has been observed earlier [24,25]. This is because of the combined effect of lesser cement taking part in the hydration reaction, and the cement replacement materials using lesser amount of water for hydration. The paste with 5% cement replacement by glass powder exhibits a w_n very close to that of the plain paste at later ages. Further examination of Fig. 4a and b shows that the non-evaporable water content per unit mass of binder is higher for pastes modified with glass powder than those with fly ash. This is an indication that glass powder modified pastes are using more water for hydration than fly ash modified pastes, at similar mass replacements. It can possibly be a result of the increased cement hydration due to the presence of glass powder (because of higher effective w/cm resulting from the low water absorption of glass). The w_n of glass powder modified pastes remains constant after 28 days, indicating that minimal secondary hydration occurs after this time, and most of the enhancement is due to increased hydration of cement. From Fig. 4b, fly ash modified pastes show increasing w_n after 28 days, indicating secondary hydration reaction.

3.3.1. Change in non-evaporable water content due to the presence of a cement replacement material

The addition of a secondary cementing material (or a filler) in cement pastes results in changes in non-evaporable water content of the paste. It is difficult to experimentally determine the change in non-evaporable water content due to the addition of a cement replacement material because the water associated with the reaction of the replacement material is difficult to separate from that of cement hydration. In this section, a simple model is presented to isolate the change in w_n due to the addition of a cement replacement material.

The total non-evaporable water (w_n)_T of a cement paste incorporating cement replacement materials can be expressed as:

$$(w_n)_T = (w_n)_c m_c + (w_n)_r m_r \quad (1)$$

where $(w_n)_c$ and $(w_n)_r$ are the non-evaporable water contents of the cement and replacement material respectively, and m_c and

m_r are their mass fractions. If the replacement material is purely a filler, then $(w_n)_r = 0$.

A cement replacement material in a paste system might facilitate an enhancement in the hydration of the available cement grains in addition to its own hydration. In such a case, the non-evaporable water content of the cement can be stated as:

$$(w_n)_c = (w_n)_{c-0} + (w_n)_{c-r} \quad (2)$$

$(w_n)_{c-0}$ is the non-evaporable water content of a cement paste with no cement replacement material, and $(w_n)_{c-r}$ is the non-evaporable water content as a result of the enhancement in cement hydration due to the presence of the replacement material. $(w_n)_c = (w_n)_{c-0}$ when there is no replacement material present in the system.

Eq. (1) then becomes:

$$(w_n)_T = [(w_n)_{c-0} + (w_n)_{c-r}]m_c + (w_n)_r m_r. \quad (3)$$

The above equation can be restated as:

$$(w_n)_T - (w_n)_{c-0}m_c = (w_n)_{c-r}m_c + (w_n)_r m_r. \quad (4)$$

The right hand side of Eq. (4) gives an expression for the change in non-evaporable water content in a modified paste $[(\Delta w_n)_r]$ as a result of the hydration of the cement replacement material and the enhancement in hydration of the cement grains resulting from the presence of the replacement material.

$$(\Delta w_n)_r = (w_n)_{c-r}m_c + (w_n)_r m_r. \quad (5)$$

$(\Delta w_n)_r$ provides an indication of the combined effects of enhancement in cement hydration due to increased effective w/c in a paste modified with a filler, and the secondary hydration in a paste modified with a pozzolanic material. Since all the terms in the left hand side of Eq. (4) are known, determination of $(\Delta w_n)_r$ is straightforward. For a plain paste, $(\Delta w_n)_r$ will always be zero. It should be noted here that $(\Delta w_n)_r$ does not separate the individual effects of enhancement in hydration and secondary reaction.

For cement replacement materials like glass powder that does not absorb too much of water at early ages, the influence of $(w_n)_{c-r}$ is likely to be more prominent in $(\Delta w_n)_r$. At later ages, the effect of $(w_n)_r$ will dominate if the replacement material is pozzolanic. When the $(\Delta w_n)_r$ values decrease with time after a certain age (this happens when the effect of enhancement in cement hydration, if any, due to the replacement material, $(w_n)_{c-r}$ diminishes, and the pozzolanic reaction does not compensate for that reduction), it can then be taken as an indication that the replacement material is not effective in the system during those times. A $(\Delta w_n)_r$ of less than zero means that $(w_n)_T$ is less than $(w_n)_{c-0} \cdot m_c$, which also shows that the replacement material is not effective at that age.

Figs. 5a and b show the values of $(\Delta w_n)_r$ plotted against hydration age for the glass powder and fly ash modified pastes. In Fig. 5a, until about 14 days, the $(\Delta w_n)_r$ values of the pastes modified with 10% and 20% glass powder increase, indicating increased hydration of the cement grains because of the higher effective w/c. Beyond 14 days, $(\Delta w_n)_r$ is seen to decrease, showing that the secondary reaction of the replacement material, if any, is not compensating for the dilution effect. However, for

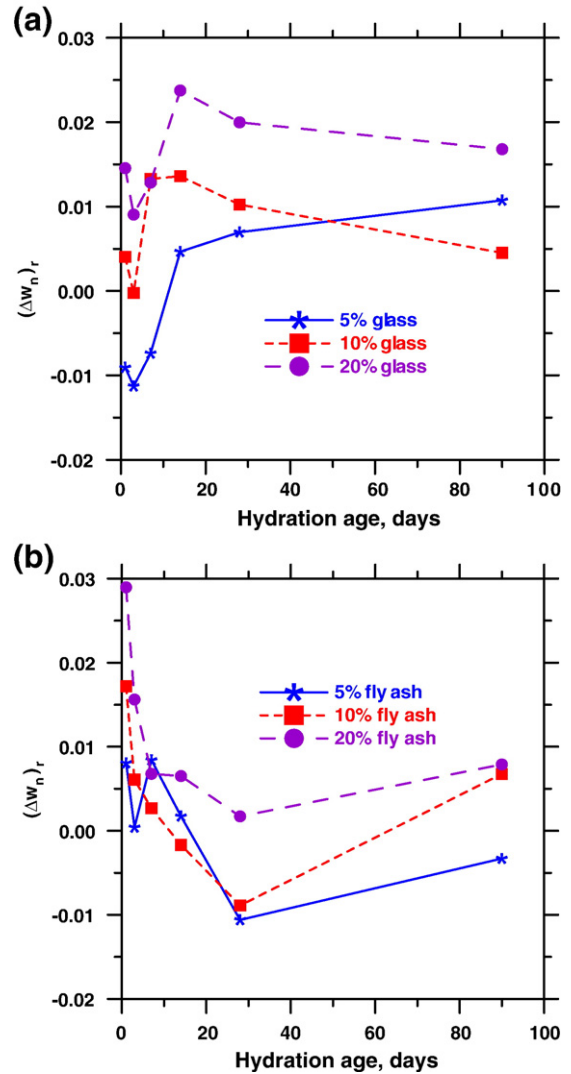


Fig. 5. Change in non-evaporable water contents as a result of replacement material hydration for pastes with (a) glass powder, and (b) fly ash.

the paste modified with 5% glass powder, $(\Delta w_n)_r$ increases consistently with time. This shows that a 5% replacement of cement with glass powder, at a w/cm of 0.42, can be considered to be effective. From Fig. 5b, it can be inferred that 10% and 20% replacement of cement with fly ash shows a beneficial effect at later ages, which is attributable to the secondary reaction.

3.3.2. Change in w_n for high w/cm pastes hydrated for a longer time

Fig. 6 depicts the change in non-evaporable water content $[(\Delta w_n)_r]$ of 0.80 w/cm glass powder and fly ash modified pastes hydrated for 140 days (these pastes were used to facilitate degree of hydration determination of 0.42 w/cm pastes). For the 5% glass powder modified paste, the $(\Delta w_n)_r$ value is higher than that of the 5% fly ash modified paste, similar to the trend of the 0.42 w/cm pastes with 5% cement replacement that are shown in Fig. 5. From Eq. (5), it is obvious that the enhancement in cement hydration is responsible for the higher $(\Delta w_n)_r$ value of glass powder, since the term $(w_n)_r m_r$ is expected to be very small (both because $(w_n)_r$ and m_r are small). However, for 10

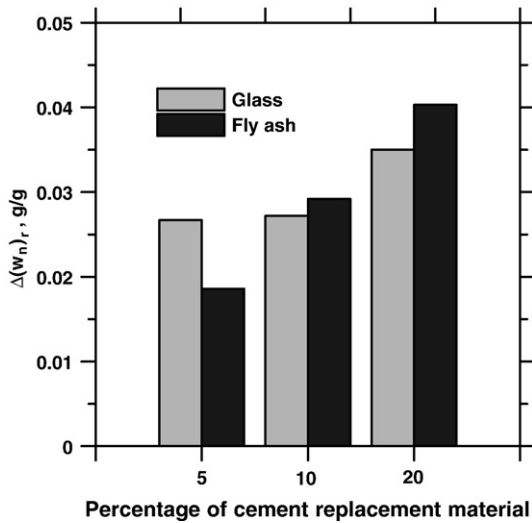


Fig. 6. Change in non-evaporable water content for high w/cm pastes.

and 20% replacement levels, the $(\Delta w_n)_r$ value is higher for the fly ash modified paste, and the difference is larger for 20% replacement level. This indicates that pozzolanic reaction is dominant in those mixtures.

3.4. Degree of hydration

3.4.1. Modeling the degree of hydration of pastes with more than one cementing material

In pastes containing one or more cement replacement materials, quantification of cement hydration and the replacement material reaction is rendered difficult by the same reason that was given in an earlier section — that it is difficult to separate the bound water contents associated with both the reactions. The degree of reaction of fly ash has been experimentally determined using a selective dissolution procedure [26,27], which is based on the principle that the hydration products of cement and fly ash, and the unreacted cement could be dissolved, leaving behind the unreacted fly ash [27]. A model that uses the amount of calcium hydroxide, the porosity of the hardened cement paste, chemical composition of cement and fly ash, and the lime–silica ratio in the cement and fly ash hydration products to determine the hydration degree of cement and pozzolanic reaction degree of fly ash has been reported [28]. However, this is an involved procedure requiring the determination of the above mentioned parameters which are quite complex. Therefore this section details the development of a model based on mixing equation for the total degree of hydration in pastes containing cement replacement materials. The degrees of hydration of cement and the replacement material cannot be separated using this method; rather it provides the overall degree of hydration of the binder in the paste.

Using an equation of the form similar to Eq. (1) for the combined degree of hydration of the paste (α_T) incorporating the replacement material,

$$\alpha_T = \alpha_c m_c + \alpha_r m_r \quad (6)$$

where α_c and α_r are the degrees of hydration of the cement and the replacement material respectively.

Representing the degrees of hydration in terms of the non-evaporable water contents results in Eq. (6) being stated as:

$$\alpha_T = \left[\frac{(w_n)_c}{(w_n)_{c-\infty}} \right] m_c + \left[\frac{(w_n)_r}{(w_n)_{r-\infty}} \right] m_r \quad (7)$$

where $\alpha_T = \frac{(w_n)_T}{(w_n)_{T-\infty}}$.

$(w_n)_{T-\infty}$, $(w_n)_{c-\infty}$, and $(w_n)_{r-\infty}$ are the ultimate non-evaporable water contents (at complete hydration) of the mixture, plain cement, and the replacement material respectively.

Substituting Eq. (2) in Eq. (7) gives:

$$\alpha_T = \left[\frac{(w_n)_{c-0} + (w_n)_{c-r}}{(w_n)_{c-\infty}} \right] m_c + \left[\frac{(w_n)_r}{(w_n)_{r-\infty}} \right] m_r. \quad (8)$$

From Eq. (4), $(w_n)_{c-r}$ can be expressed as:

$$(w_n)_{c-r} = \frac{(w_n)_T}{m_c} - (w_n)_{c-0} - (w_n)_r \frac{m_r}{m_c}. \quad (9)$$

Substituting Eq. (9) in Eq. (8) and rearranging the terms give α_T as:

$$\alpha_T = \frac{(w_n)_T}{(w_n)_{c-\infty}} + (w_n)_r m_r \left[\frac{1}{(w_n)_{r-\infty}} - \frac{1}{(w_n)_{c-\infty}} \right]. \quad (10)$$

The above expression is a concise means of representing the combined degree of hydration of pastes containing cement replacement materials. This equation accounts for the enhancement in the degree of hydration which may be the result of a higher effective w/c when non-reactive fillers are used, and the degree of hydration of the supplementary cementing material. This expression could be modified to account for more than one cement replacement material.

3.4.2. Experimentally measured overall degree of hydration

The degrees of hydration of the modified pastes were experimentally determined from the w_n of the chosen pastes and the w_n of the pastes made with w/cm of 0.80 which were cured for a much longer duration (140 days). The experimentally determined degrees of hydration are shown in Fig. 7a and b for glass powder and fly ash modified pastes respectively. It can be seen that the overall degrees of hydration are lower for most of the modified pastes. This could be easily explained using Eq. (7). The first term on the right hand side of this equation is reduced because of the reduced cement content, and since w_n of the replacement material is lower than that of cement (Section 3.3), the second term is not able to compensate for the reduction. While the measured degrees of hydration for glass powder modified pastes plateaus after 28 days, for the fly ash modified pastes, the values are found to increase, which is expected.

3.4.3. Predicting degrees of hydration using the model

The total non-evaporable water contents of the pastes $(w_n)_T$ have been determined experimentally and shown in Fig. 4a and b. The Bogue composition of the cement calculated using the oxide contents, along with the reported chemically bound water contents of the compounds [29] was used to calculate the ultimate

non-evaporable water content of cement $(w_n)_{c-\infty}$, which for this cement is 0.227. The ultimate non-evaporable water content of fly ash is taken as 0.05 [30]. Though it can be seen from Fig. 4 that the non-evaporable water contents of glass powder modified pastes are higher than those of fly ash modified pastes, it is mostly the result of enhancement in cement hydration, and not necessarily due to increased secondary reaction of glass powder. Hence the ultimate non-evaporable water content attributable to glass powder is also assumed to be 0.05.

It is well known that fly ash hydration in cement pastes begins only after a certain period of time. Hence $(w_n)_r$ values are taken as zero until 14 days, so that Eq. (10) is simplified. After that, the pozzolanic reaction is mainly responsible for the change in non-evaporable water content. Hence, from Eq. (5), $(w_n)_r m_r = (\Delta w_n)_r$. Similarly, for glass powder modified pastes, Fig. 4a shows that, for higher replacement levels at later ages, there is little indication of secondary reaction. Hence the $(w_n)_r$ values for those mixtures, at those times can be neglected. Since the mass fraction of the replacement material also is lower, the term $(w_n)_r m_r$ is very small.

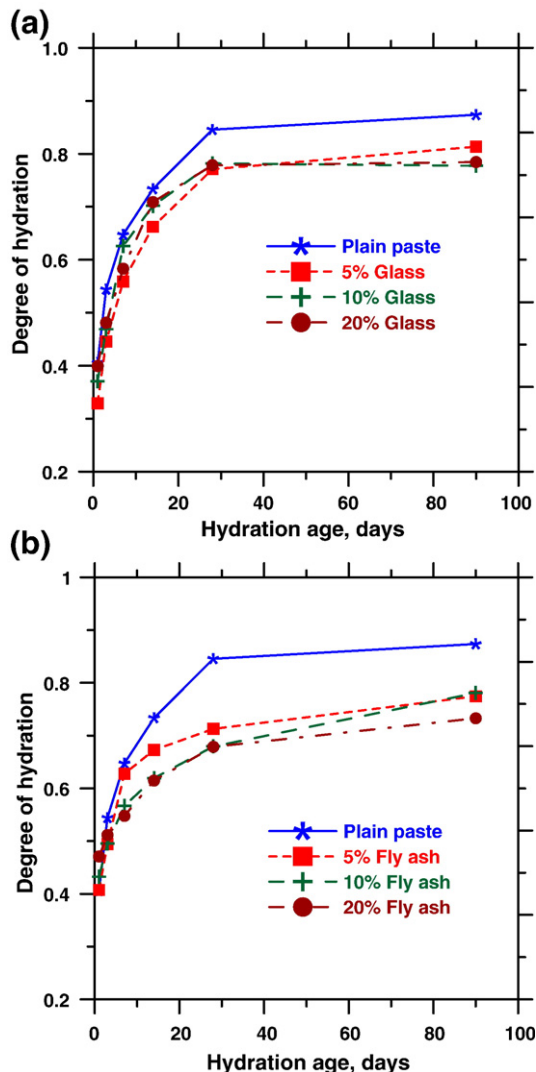


Fig. 7. Experimentally determined degrees of hydration of plain and (a) glass powder and (b) fly ash modified cement pastes.

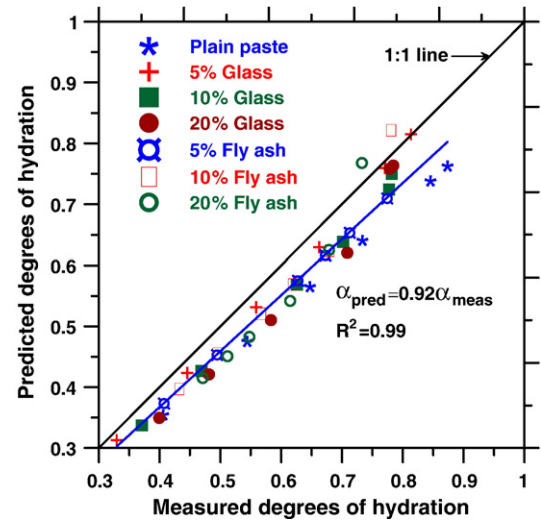


Fig. 8. Experimentally measured and predicted degrees of hydration.

3.4.4. Comparison of the measured and predicted degrees of hydration

A comparison of the experimentally determined and predicted degrees of hydration of all the pastes used in this study is shown in Fig. 8. There is good agreement between measured and predicted values (R^2 of 0.99), even though the predicted values are lower than the measured degrees of hydration by about 8%. One reason for this could be the following. For experimentally determined degrees of hydration, the w_n values of the pastes are divided by w_n of high w/cm pastes at complete hydration (140 days). At this time, the hydration of the cementing materials is not complete in the high w/cm paste, as evidenced by a measured non-evaporable water content of 0.192 for the plain cement paste instead of the value being closer to 0.227, thus leading to lower w_n values and consequently, higher measured degrees of hydration of the pastes at varying ages. The assumptions used in arriving at the values of $(w_n)_r$ and $(w_n)_{r-\infty}$ in the model could have also contributed to the discrepancy. Using the experimentally obtained value of $(w_n)_{c-\infty}$ in Eq. (10) instead of 0.227 has been found to bring the data points closer to the 1:1 line in Fig. 8.

4. Conclusions

This paper has evaluated the influence of a fine glass powder on cement hydration. The pozzolanicity of the cement replacement materials, the alkali release characteristics from glass powder, and the non-evaporable water contents of the hydrated pastes were experimentally determined. A model has been developed to predict the degree of hydration of pastes containing supplementary cementing materials or hydration enhancing fillers.

The fine glass powder was found to exhibit pozzolanicity levels equal to or greater than that of fly ash at all the ages studied. The strength activity index of a coarser variety of glass powder was also investigated so as to bring out the changes in pozzolanic behavior of the glass powder with change in particle sizes.

Using flame emission spectroscopy and electrical conductivity studies, it has been shown that the glass powder releases only

a small fraction of alkalis into the pore solution. The amount of sodium released is insufficient to accelerate the setting or increase the early age strength of cement pastes, as was observed from a companion study [15].

In general, the non-evaporable water contents of modified pastes were found to be lower than that of the plain paste. The glass powder modified pastes showed higher non-evaporable water contents than the fly ash modified pastes of the same replacement level of cement, because of the enhancement in cement hydration. An expression has been developed for the change in non-evaporable water content, $(\Delta w_n)_r$, as a result of enhancement in cement hydration and the hydration of the cement replacement material. This term serves as an indicator of the combined effects of enhancement in cement hydration in a paste modified with a filler, and the secondary hydration in a paste modified with a pozzolanic material, and can be used as an index for the efficiency of any cement replacement material in the paste system. A decrease in this value with time indicates that the replacement material is not contributing in the matrix. This is observed for pastes modified with high replacement levels of glass powder, where as pastes with low replacement levels show beneficial effect. It is seen that the $(\Delta w_n)_r$ values of fly ash modified pastes increase after 28 days, indicating secondary reaction.

A model based on a mixture equation is developed in this paper to determine the combined degree of hydration of pastes modified with cement replacement materials. The non-evaporable water contents of plain and modified pastes at various ages, the ultimate non-evaporable water contents of the replacement materials, and the mass fraction of the replacement materials are the only parameters required to predict the combined degree of hydration. Degrees of hydration determined from the model agree well with those measured experimentally.

Acknowledgments

The authors thank the Empire State Development Program of New York State for the support extended to this study. The help from Woodruff Block Company, Graymont Materials, and Potters Industries is also appreciated.

References

- [1] W. Jin, C. Meyer, S. Baxter, Glascrete — concrete with glass aggregates, *ACI Mater. J.* 97 (2) (2000) 208–213.
- [2] A. Shayan, A. Xu, Value-added utilization of waste glass in concrete, *Cem. Concr. Res.* 34 (2004) 81–89.
- [3] C. Meyer, N. Egosi, C. Andela, Concrete with waste glass as aggregate. In: Recycling and reuse of glass cullet. Proceedings of the international symposium, March 2001. Concrete technology unit of ASCE and University of Dundee.
- [4] I.B. Topcu, C. Canbaz, Properties of concrete containing waste glass, *Cem. Concr. Res.* 34 (2004) 267–274.
- [5] C.M. Sangha, A.M. Alani, P.J. Walden, Relative strength of green glass cullet concrete, *Mag. Concr. Res.* 56 (5) (2004) 293–297.
- [6] S.B. Park, B.C. Lee, J.H. Kim, Studies on mechanical properties of concrete containing waste glass aggregate, *Cem. Concr. Res.* 34 (2004) 2181–2189.
- [7] G. Chen, H. Lee, K.L. Young, P.L. Yue, A. Wong, T. Tao, K.K. Choi, Glass recycling in cement production — an innovative approach, *Waste Manage.* 22 (2002) 747–753.
- [8] Z. Xie, Y. Xi, Use of recycled glass as a raw material in the manufacture of Portland cement, *Mater. Struct.* 35 (2002) 510–515.
- [9] N. Neithalath, N. Schwarz, Cement pastes incorporating coarse glass powder hydration, strength, and heat development, *Mater Struct.* in press.
- [10] N. Schwarz, M. DuBois, N. Neithalath, Electrical conductivity based characterization of plain and coarse glass powder modified cement pastes, *Cem. Concr. Compos.* 29 (2007) 656–666 2007.
- [11] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glass, *Cem. Concr. Res.* 30 (2000) 91–100.
- [12] C. Shi, Y. Wu, C. Riefler, H. Wang, Characteristics and pozzolanic reactivity of glass powders, *Cem. Concr. Res.* 35 (2005) 987–993.
- [13] A. Shayan, A. Xu, Performance of glass powder as a pozzolanic material in concrete: a field trial on concrete slabs, *Cem. Concr. Res.* 36 (2006) 457–468.
- [14] T.D. Dyer, R.K. Dhir, Chemical reactions of glass cullet used as cement component, *ASCE J. Mater. Civ. Eng.* 13 (6) (2001) 412–417.
- [15] N. Schwarz, N. Neithalath, Quantifying the cementing efficiency of fine glass powder and its comparison to fly ash, *Proceedings of the 1st International Conference on Recent Advances in Concrete Technology '07*, Washington D.C., September 2007.
- [16] M.P. Luxan, F. Madruga, J. Saavedra, The evaluation of pozzolanic activity of natural products by conductivity measurement, *Cem. Concr. Res.* 19 (1989) 63–68.
- [17] I. Jawed, J. Skalny, Alkalis in cement: a review II. Effects of alkalis on hydration and performance of Portland cement, *Cem. Concr. Res.* 8 (1978) 37–52.
- [18] V.S. Ramachandran, J.J. Beaudoin, S.L. Sarkar, X. Aimin, Physico-chemical and microstructural investigations on the effect of NaOH on the hydration of 3CaO·SiO₂, II, *Cemento* 2 (1993) 73–84.
- [19] M.C.G. Juenger, H.M. Jennings, Effects of high alkalinity on cement pastes, *ACI Mater. J.* 98 (3) (2001) 251–255.
- [20] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, *Cem. Concr. Res.* 29 (1999) 159–170.
- [21] B.J. Christensen, R.T. Coverdale, R.A. Olson, S.J. Ford, E.J. Garbocz, H.M. Jennings, T.O. Mason, Impedance spectroscopy of hydrating cement based materials: measurement, interpretation and application *J. Amer. Cer. Soc.* 77 (1994) 2789–2804.
- [22] N. Neithalath, J. Weiss, J. Olek, Characterizing enhanced porosity concrete using electrical impedance to predict the acoustic and hydraulic performance, *Cem. Concr. Res.* 36 (2006) 2074–2085.
- [23] W.J. McCarter, G. Stars, T.M. Chrisp, Immittance spectra for portland cement/fly ash based binders during early hydration, *Cem. Concr. Res.* 30 (1999) 377–387.
- [24] N. Neithalath, Cement pastes incorporating coarse glass powder filler, *Proceedings of International Conference on Sustainable Construction Materials and Technologies*, Coventry, UK, June 2007.
- [25] J.K. Weng, B.W. Langan, M.A. Ward, Pozzolanic reaction in portland cement, silica fume, and fly ash mixtures, *Can. J. Civ. Eng.* 24 (1997) 754–760.
- [26] L. Lam, Y.L. Wong, C.S. Poon, Degree of hydration and gel/space ratio of high-volume fly ash/cement systems, *Cem. Concr. Res.* 30 (2000) 747–756.
- [27] S. Ohsawa, K. Asaga, S. Goto, M. Daimon, Quantitative determination of fly ash in the hydrated fly ash — CaSO₄·2H₂O–Ca(OH)₂ system, *Cem. Concr. Res.* 15 (1985) 357–366.
- [28] A. Wang, C. Zhang, W. Sun, Fly ash effects II. The active effect of fly ash, *Cem. Concr. Res.* 34 (2004) 2057–2060.
- [29] A.M. Neville, *Properties of Concrete*, 4th Edition, Addison Wesley Longman Limited, Essex, England, 1996.
- [30] E. Garcia, Non-evaporable water from neat OPC and replacement materials in composite cements hydrated at different temperatures, *Cem. Concr. Res.* 33 (2003) 1883–1888.