Investigations on the Influence of Coarse Glass Powder on the Properties of Cement Paste Using Electrical Impedance

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Abstract

This paper uses electrical conductivity and the microstructural features that can be derived from electrical conductivity to understand the influence of coarse glass powder on the properties of cement pastes. It is observed that the glass powder addition improves the hydration of cement grains. However, this advantage is negated by the reduced amount of hydration products in modified pastes, i.e. the dilution effect. The reduction in compressive strengths and the increase in porosity of the modified pastes confirm this effect. The variation of electrical conductivity and its derivative with time can be related to the various phases in the microstructural development of the paste. It is observed that the addition of glass powder results only in minor changes in the setting time of the pastes. The conductivities of the paste pore solutions are determined from ionic concentration using Taylor's model. A parallel model for electrical conductivity has been used to extract the pore connectivity factor. Using the porosity and pore connectivity factor, a unique term called the characteristic efficiency factor is proposed, which provides an indication of the microstructure of the modified pastes with respect to that of the plain paste.

1.0 Introduction

With the advent of self-consolidating concretes (SCC), and high performance concretes (HPC), there has been considerable interest in the use of non-standard fine materials in concrete. In SCC, these fine materials are added so as to increase the flowability of concrete, at the same time aiding to reduce the cement content. This is an economically viable proposition, and also helps to control thermal and shrinkage stresses. In HPC, which are proportioned with a substantially reduced water-to-cement ratio (w/c), it is well known that not all the cement in the mixture hydrates. Replacement of coarser cement particles that do not hydrate completely with inert filler materials in such mixtures can lead to: (i) reduction in overall cement consumption, and (ii) new avenues for the use of non-standard filler materials and better means of disposal of these materials.

This paper investigates the influence of a coarse glass powder on the properties of cement pastes. The glass powder is a waste product from the manufacture of industrial application and highway safety glass beads. Incorporation of such a powder in concrete, provided it is not detrimental to the properties and performance of concrete, becomes an environment-friendly option in regions where there are local sources of glass powder which needs to be safely disposed. Understanding the influence of glass powder on the properties of cement paste and concrete is expected to help in the development of optimal mixture proportions using this material. This, in turn, can lead to increased avenues of using glass powder, and consequently a sustainable and economical method of waste disposal.

A few studies have reported the use of glass powder in concrete, which focuses primarily on the pozzolanicity and strength development of mortars and concrete incorporating fine glass powder [1-3]. In this paper, investigations are carried out on cement pastes containing coarse glass powder using electrical impedance methods. Electrical property measurements are well recognized as powerful tools for continuous monitoring of the microstructural development of cement based materials [4-7]. These measurements take advantage of the fact that as cement hydrates, the volume and the connectivity of the pore network, as well as the concentration and conductivity of the pore solution, changes with time.

2.0 Experimental Program

2.1 Materials and Mixtures

The cement pastes investigated in this study were made using Type I ordinary portland cement conforming to ASTM C 150. The coarse glass powder was a waste material from an industrial glass bead manufacturing facility. The size distribution of the glass powder is such that 60% is finer than 88 μm. The Na_2O content in glass powder is very high (13.7%) compared to that of cement (0.19%). Plain cement pastes as well as pastes where a certain amount of cement is replaced by glass powder were made. The modified pastes were made with glass powder replacing 10, 20, and 30% cement by mass. The water-to-solids (cement + glass powder) ratio (w/s) used was 0.42.

Cement and glass powder were mixed dry in a laboratory mortar mixer for 2 minutes. Water was then gradually added and mixed further for 3 minutes. After this time, specimens were prepared for flow value determination, electrical impedance measurements, compressive strength tests, and non-evaporable water content estimation. Compressive strength was determined on 50 mm cube specimens, according to ASTM C 109.

2.2 Determination of Degree of Hydration Using Non-Evaporable Water Content

Non-evaporable water content (w_n) is used in this paper as a measure of the degree of hydration. It is determined from the mass of a paste sample heated first to 105°C (w_{105}) for 24 hours, and then to 1050 °C (w_{1050}) for 3 hours as:

$$w_n = \frac{w_{105} - w_{1050}}{w_{1050}} \qquad (1)$$

The non-evaporable water contents of plain pastes were converted into degrees of hydration by dividing them by the w_n of a completely hydrated paste (taken as 0.24), and correcting for the loss of ignition of the dry cement. Since the glass powder is just a filler, the obtained degrees of hydration were corrected using the mass fraction of cement in the mixtures to give actual degrees of hydration (α_{act}) as shown in Eq. 2.

$$\alpha_{act} = Min\left\{1, \frac{\alpha}{(1 - g/100)}\right\} \qquad (2)$$

The minimum function is used to avoid the possibility of α_{act} obtaining values greater than 1.0. The original w/s were also corrected to the effective water-cement ratios $(w/c)_{eff}$ by using just the mass of cement.

2.3 Determination of Specimen Conductivity using Electrical Impedance

Electrical impedance tests on cement pastes were carried out using an HP 4284A LCR meter which was connected to a personal computer for data acquisition. Immediately after mixing, the cement pastes were placed in 50 mm x 50 mm x 150 mm acrylic molds. Stainless steel plates, 0.75 mm thick were placed at the ends of the molds to be used as electrodes. The impedance measurements were carried out using a 250 mV AC signal over a frequency range of 20 Hz to 1 MHz. In a typical Nyquist plot from electrical impedance measurements, which is the plot of the real part of the impedance against the imaginary part, two arcs are observed – the high frequency bulk arc corresponding to the sample, and a low frequency electrode arc. The point where these two arcs meet is considered to the bulk resistance of the sample (R_b). The effective conductivity (σ_{eff}) is obtained from the bulk resistance (R_b), the specimen length l, and the cross-sectional area A as:

$$\sigma_{eff} = \frac{l}{R_b A} \qquad (3)$$

3.0 Results and Discussions

3.1 Electrical Conductivity Response of Plain and Modified Cement Pastes

The variation of electrical conductivity with time for plain and glass powder modified cement pastes is shown in Fig.1. The primary Y-axis of the figure shows the effective electrical conductivity determined using Eq.3, where as the secondary Y-axis shows the time derivative of the conductivity ($\frac{d\sigma_{eff}}{dt}$).

From Fig.1, it can be noticed that, immediately after mixing and at very early times (of the order of a few hours), the conductivity of the plain paste is the highest. As more and more cement is replaced with glass powder, the effective conductivities decrease. The lowest conductivity is observed for the mixture having the highest cement replacement with glass powder. This could be because of either or both of the following factors: (i) effective conductivity of cement pastes is a function of the pore volume. By using glass powder which has a lower specific gravity (2.50, as compared to 3.15 of cement) as a cement replacement material by mass, the overall solid volume in the mixture at very early times (of the order of a few hours) increases, thus reducing the porosity, and (ii) the reduction in the amount of conductive ions released by the particulate phases, brought about by the reduction in cement content, soon after mixing with water. Although the Na_2O content of the glass powder is higher, it is conceivable that the glass powder is not releasing Na^+ ions into the pore solution soon after coming into contact with water. The conductivities of all the pastes increase till about 1.5 hours, after which they start to decrease. The initial setting time of the pastes occur in the suddenly dropping part of the conductivity-time plot, when the solid phases have begun to form in the material, and the pore phase depercolates. After about 24 hours, no drastic change in the effective conductivity is observed. The pore structure has become very tortuous at this stage.

The representation of the time derivative of effective conductivity reveals several peaks and troughs, which can be related to various microstructural development phases in the pastes. The first trough in the derivative plot can be related to the end of the dissociation period. From Fig.1, the time at which this appears is the same (1.44 hours) for all the pastes. The time corresponding to the first peak in the derivative curve can be thought of as the initial setting time. The period between the first peak and the second trough coincides with the acceleration phase in the heat evolution curve. From an analysis of the various characteristic features of Fig.1, it can be concluded that the addition of glass powder does not significantly alter the setting time or the time at which solid hydration products begin to form. More details can be found in [8].

3.2 Degree of Hydration and Porosity of Plain and Modified Pastes

The actual degrees of hydration α_{act} (degree of hydration of the active particles, i.e., cement grains) determined using the procedure outlined in Section 2.2 are shown in Fig.2. The degrees of hydration increase with increase in glass powder content because of the increase in effective water-cement ratio of the system. The enhancement in degree of hydration is noticed for all ages. However, it is unlikely that the increased degrees of hydration manifested in Fig.2 would cause any increase in the total volume of hydrated products in a unit volume of the system because of the reduction in cement content. The replacement of cement by glass powder causes a dilution effect. Optimization of mixture proportions so that the increased degree of hydration accounts for the dilution effect is a crucial step in designing better performing mixtures with non-reactive fillers. Such an attempt for coarse glass powder modified mixtures will be elaborated in a separate study.

From the actual degrees of hydration, the porosity (ϕ_{pore}) of the pastes can be obtained as [9]:

$$\phi_{pore} = \frac{\rho_{cem}(w/c)_{eff} - f_{exp}\alpha_{act}}{1 + \rho_{cem}(w/c)_{eff} + \frac{\rho_{cem}}{\rho_{glass}}(g/c)} \tag{4}$$

ρ_{cem} and ρ_{glass} are the specific gravities of the cement (3.15) and glass powder (2.50) respectively, f_{exp} is the volumetric expansion coefficient for the solid cement hydration products relative to the cement (2.15-1=1.15), and g/c is the glass powder to cement ratio by mass. $(w/c)_{eff}$ is the effective water-cement ratio, which for a w/s of 0.42 and 20% replacement of cement by glass powder, is 0.525.

Fig.3 depicts the variation of porosity with age for plain and modified pastes at the ages of 1,3,7,14, and 28 days. Increasing the glass powder content in the mixtures result in an increase in porosity at all ages, which can be attributed to the fact that the dilution effect is not compensated by the increase in actual degree of hydration. The porosities of glass powder modified pastes ($\phi_{modified}$) can be adequately represented as a function of the porosities of the plain paste (ϕ_{plain}) at the same age as:

$$\phi_{modified} = \phi_{plaim}(1 + 0.002G) \quad \text{(for early ages: 1, 3, and 7 days)} \tag{5}$$

$$\phi_{modified} = \phi_{plaim}(1 + 0.0035G) \quad \text{(for later ages: 14, and 28 days)} \tag{6}$$

where G is the percentage of glass powder replacing cement in the mixture. The R^2 values for the fits in Fig.3 range from 0.89 to 0.99.

The constants in Eqs.5 and 6 indicate that the porosity of the modified mixtures increases at a faster rate at later ages than at early ages. At early ages, when the degree of hydration is low, the filler effect of the coarse glass powder compensates to a certain extent for the reduction in volume of hydrated products, where as at later ages, this effect is non-existent, leading to the observation mentioned above. In other words, the effect of dilution is more prominent at later ages.

3.3 Compressive Strength of the Modified Pastes

Incorporation of coarse glass powder in cement pastes is found to decrease the compressive strength of the pastes as shown in Fig.4. The reduction in cement content and an increase in effective water-cement ratio are the reasons for this behavior. The reduction in compressive strength with increasing glass powder content can be related to the increase in porosity (Fig.3) of the glass powder modified systems.

In order to understand the reduction in compressive strength of glass power modified pastes relative to that of plain paste, the normalized strength (ratio of compressive strength at a certain glass powder content $f'_{c\text{-modified}}$, to that of the plain paste $f'_{c\text{-plain}}$) is plotted against the glass powder content in Fig.5. The strength of the modified paste at any age can be related to the percentage of glass powder replacing cement (G) and the strength of plain paste at that age as:

$$f'_{c-\mathrm{mod}\,ifed} = f'_{c-plain}(1-0.02G) \tag{7}$$

This gives an easy-to-use first approximation for the compressive strength of coarse glass powder modified cement pastes. This also allows the determination of the amount of glass powder to be used as a cement replacement for a certain desired strength.

3.4 Development of a Characteristic Efficiency Factor Based on Electrical Conductivity Measurements

Using a modified parallel model, the effective electrical conductivity of cement pastes (σ_{eff}) can be estimated as a function of the pore solution conductivity (σ_{pore}), porosity (ϕ_{pore}), and the pore connectivity factor (β) as [10]:

$$s_{eff} = s_{pore} f_{pore} b \tag{8}$$

The effective conductivity at any age can be obtained from Eq.3. The porosity (ϕ_{pore}) can be estimated from the determined degrees of hydration using Eq.4. The only other parameter needed to determine the pore connectivity factor (β) is the pore solution conductivity (σ_{pore}). The next sub-section briefly describes the determination of σ_{pore}.

3.4.1 Estimation of Pore Solution Conductivity from Ionic Concentration

Experimental methods of pore solution analysis by squeezing the pore solution from hardened pastes have been reported elsewhere [11]. In this paper, the concentrations of the dominant ions (Na^+, K^+, and OH^-) in 1 day or older pastes are calculated using a procedure [12] which has been found to predict these concentrations fairly accurately. Using the concentrations of the ionic species obtained from Taylor's models [12], σ_{pore} can be estimated using Equation 9:

$$\sigma_{pore} = \sum \frac{z_i \lambda_i^0 c_i}{1 + G_i I_M^{0.5}} \tag{9}$$

where z_i is the valence, λ_i^0 is the equivalent conductivity at infinite dilution, the values of which are given in [13], c_i is the molar concentration determined using Taylor's model, G_i is an empirical coefficient, all for the species *i*. I_M is the ionic strength on a molar basis given by:

$$I_M = \frac{1}{2} \sum z_i^2 c_i \tag{10}$$

The variation of pore solution conductivity calculated using Eq.9 with the amount of glass powder replacing cement is plotted in Fig.6. It can be noticed that at early ages (1 and 3 days), σ_{pore} is practically independent of the glass powder content in the mixture, which shows that the ionic contribution to the pore solution is primarily from the cement. At later ages, σ_{pore} increases because of the increase in Na^+ ions released from the glass powder (Na_2O content in glass powder is very high, even though the K_2O content is lower than that of cement). Another reason for the higher values of σ_{pore} at later ages with increasing glass powder content is that the volume of hydration products is less in modified pastes, leading to a reduction in the amount of ions that can be incorporated into the hydration products. Majority of these ions thus remain in the pore solution.

3.4.2 Determination of Pore Connectivity Factor and Characteristic Efficiency Factor

Using the effective conductivity (σ_{eff}) obtained from Eq.3, the pore solution conductivity (σ_{pore}) determined using the procedure above and plotted in Fig.6, and the porosity (Fig.3), the pore connectivity factor (β) is determined and plotted in Fig.7 as a function of the glass powder content. At very early ages (1 and 3 days), β increases with increase in glass powder content. The reason for this behavior is the higher value of σ_{eff} at these times for the modified pastes as could be observed in Fig.1. The value of σ_{pore} at these times stay relatively constant (Fig.6) and the increase in porosity is not as drastic at these times as at later ages, which is easily observed from Eq.5 and 6. At later ages, β decreases with increase in glass powder content. During these times, the σ_{eff} of plain and modified pastes are very close to each other even when σ_{pore} and ϕ_{pore} are considerably higher for modified pastes. The un-reacted particles of the glass powder modify the pore structure of the material so as to make the electrical conduction paths more tortuous, demonstrated by a reduction in β.

In order to determine a characteristic efficiency factor (γ), the product of porosity (ϕ_{pore}) and pore connectivity factor (β) are determined for each glass powder content, and normalized by the ($\phi_{pore}\beta$) of the plain paste as shown in Eq.11.

$$\gamma = \frac{(\phi_{pore}\beta)_{\text{mod}\,ified}}{(\phi_{pore}\beta)_{plain}} = \frac{(\frac{\sigma_{eff}}{\sigma_0})_{\text{mod}\,ified}}{(\frac{\sigma_{eff}}{\sigma_0})_{plain}} \qquad (11)$$

The characteristic efficiency factor is actually the combined microstructural feature (since it combines both ϕ_{pore} and β) of the modified paste at a certain age normalized by the microstructural feature of the plain paste. It thus provides an indication of the modified paste microstructure relative to that of the plain paste. The variation of γ with age is plotted in Fig.8. The γ values are more than 1.0 for all glass powder modified pastes at early ages; higher the glass powder content, higher the γ value. This is because of an increase in porosity and pore connectivity factor of glass powder modified mixtures at early ages, the reasons for which have been elucidated earlier in this paper. At later ages, the values of γ fall below 1.0 for mixtures with higher glass powder content, which indicates that ($\phi_{pore}\beta$) is lower for the modified pastes than the plain paste, suggesting that a certain degree of pore refinement might have occurred. However, the compressive strength results from Figs.5 and 6 do not indicate any pore refinement. Even though the porosities of the modified pastes are higher, the pore connectivity factor is lower than that of the plain paste, resulting in lower ($\phi_{pore}\beta$) values for modified pastes, and thus lower γ. It is postulated at this stage that, for a supplementary cementing material which undergoes secondary reaction (unlike the inert glass powder used here as cement replacement), determination of γ will be beneficial in characterizing the efficiency of the cement replacement material. More studies to ascertain this hypothesis using finely divided glass powder that exhibits pozzolanicity is being carried out.

4.0 Conclusions

This study uses electrical conductivity and the microstructural features derivable from electrical conductivity as tools to characterize coarse glass powder modified cement pastes. The following conclusions pertain to this study and are listed below:

(i) The electrical conductivity response as well as the time derivative of conductivity has been shown to be effective in relating to the various phases in the microstructural development of plain and modified cement pastes. The addition of coarse glass powder as a cement replacement is found not to significantly affect the onset of various processes in the system.

(ii) The actual degree of hydration of the cement grains increases with glass powder addition, because of the increase in effective water content in the system. For the glass powder contents investigated in this study, the effect of dilution is more than what could be compensated by the increase in actual degree of hydration. The fact that the dilution effect is not compensated by increase in degree of hydration is reinforced by the increasing porosity with increase in glass powder content. The compressive strength of the mixtures also decreases with increase in glass powder content.

(iii) The pore solution conductivity increases with increase in glass powder dosage at later ages because of the high Na_2O content in the glass powder. Also, the reduced amount of hydration products that can sorb the alkali ions results in higher pore solution conductivity for the modified pastes. The pore connectivity factor increases with glass powder content at early ages, but decreases at later ages.

(iv) A characteristic efficiency factor that combines both porosity and pore connectivity factor, and thus is an ideal microstructural feature of the paste, is proposed. This factor provides an indication of the modified paste microstructure relative to that of the plain paste. For a supplementary cementing material which undergoes secondary reaction (unlike the inert glass powder used here as cement replacement), determination of the characteristic efficiency factor can be an ideal tool to quantify the efficiency of the supplementary material.

5.0 References

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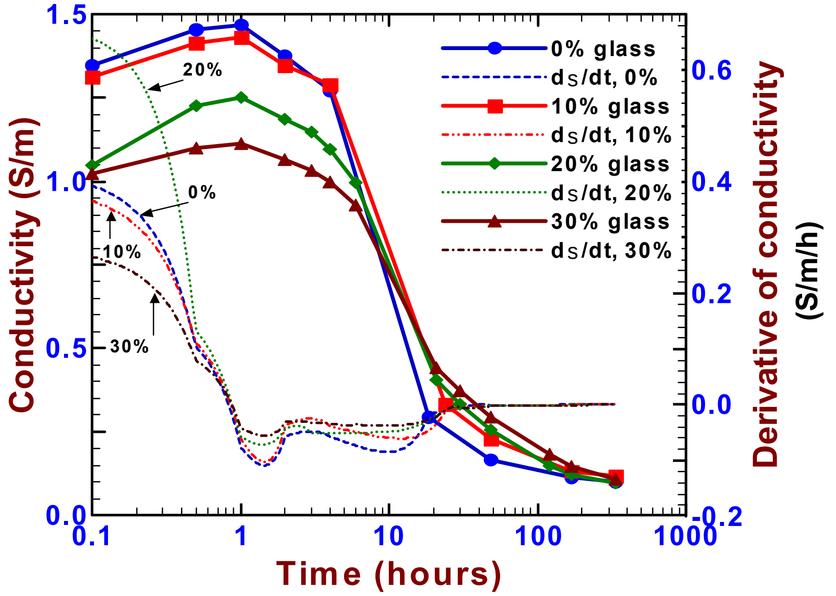
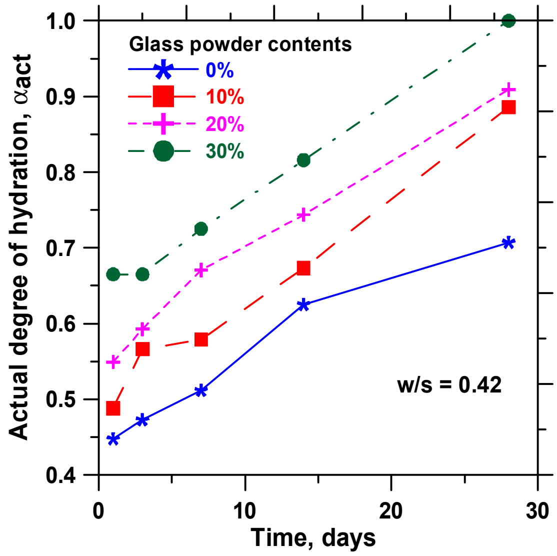


Fig.1 – Electrical conductivity and its derivative as a function of time for plain and modified pastes



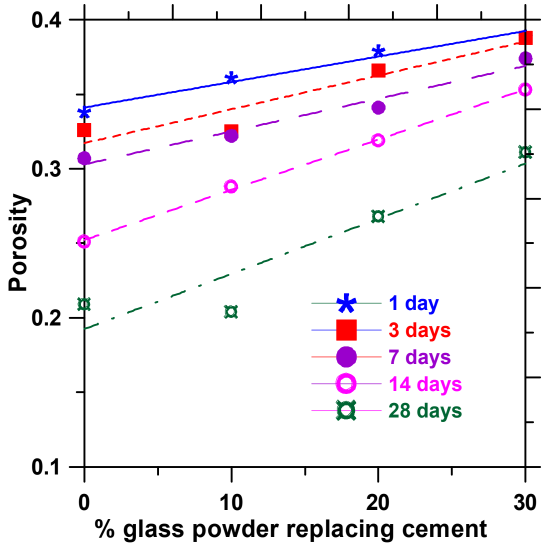


Fig.2 – Variation of degree of hydration with time

Fig.3 – Variation of porosity with glass powder content in the mixture

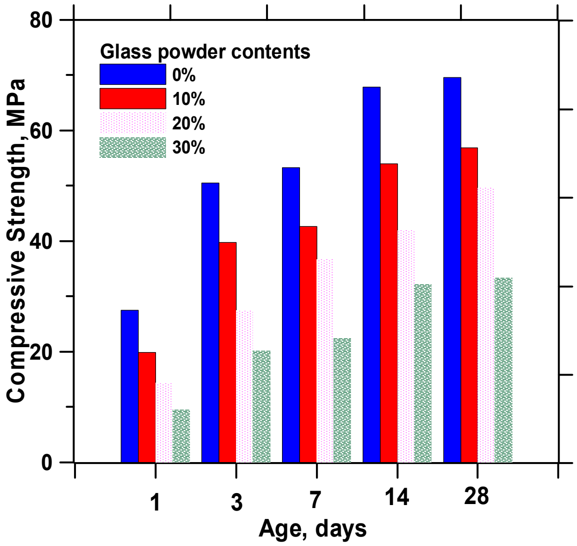


Fig.4 – Compressive strength of plain and modified pastes

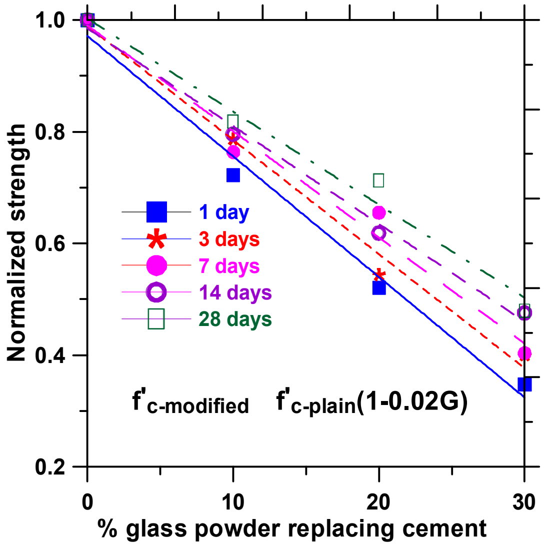


Fig.5 – Normalized compressive strength as a function of glass powder content

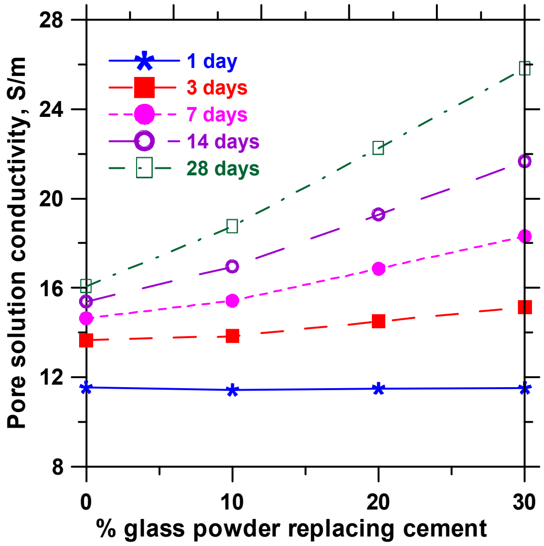


Fig.6 – Variation of pore solution conductivity with glass powder content

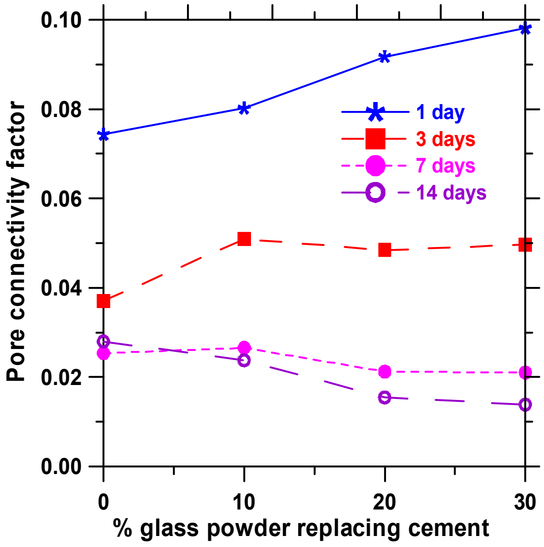


Fig.7 – Variation of pore connectivity factor with glass powder content

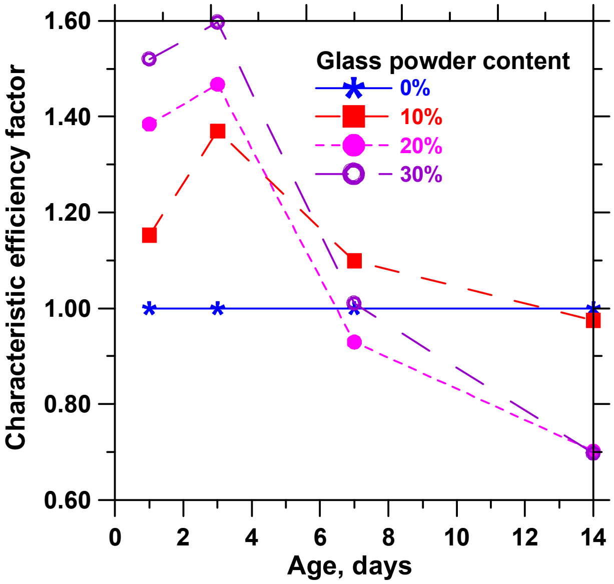


Fig.8 – Variation of characteristic efficiency factor with age