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Hydration in high-performance cementitious systems containing vitreous calcium aluminosilicate or silica fume

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ABSTRACT

The influence of a relatively new high-performance cement replacement material—vitreous calcium aluminosilicate (VCAS)—on the hydration behavior in cementitious systems, and its comparison to silica fume (SF) are presented in this paper. VCAS is shown to have no cementitious qualities, but exhibits significant pozzolanicity, which has been quantified using strength activity index and electrical conductivity change. VCAS modified pastes are found to consume more water during hydration than the corresponding SF modified pastes. Based on a normalized calcium hydroxide content defined in this paper, it is seen that the pozzolanic reaction of VCAS does not happen until 7 days while that of SF occurs as early as the first day. The degrees of hydration of the modified pastes are predicted using a model that employs the change in non-evaporable water resulting from the use of these replacement materials. VCAS modified pastes show lower later age porosities as compared to the plain and SF modified pastes. However, at equal degrees of hydration, SF modified pastes show the lowest porosity.

1. Introduction

The use of high-performance concretes (HPC) has become common in a variety of infrastructural and other applications. The production of HPCs typically requires the use of highly reactive supplementary cementing materials (SCM) in order to meet the strength and durability criteria. Silica fume (SF), which contains about 90% SiO_2 in the amorphous form is one of the most common high-performance mineral admixtures used in HPC. The influence of SF on the mechanical and durability properties of concrete is well documented. The pozzolanic reaction of SF and the influence of SF on the hydration of cement in pastes also have been discussed in various studies[1–6], and depending on the state of SF (densified or not), differing conclusions have been arrived at.

In recent years, studies on a number of other highly reactive SCMs like metakaolin and ultrafine fly ash have been reported[7–12]. Another new entrant into this class is a vitreous calcium aluminosilicate (VCAS) pozzolan, which is a patented product, manufactured by heating a blend of ground silica, lime, and alumina compounds to a molten state, followed by solidification by quenching, and final grinding. VCAS, like metakaolin, is an aluminosilicate, with a very similar SiO_2 content but a lower Al_2O_3 content. There is only one reported study on the fresh and hardened properties of concretes containing VCAS[13]. This study is therefore designed to understand the influence of VCAS on the hydration behavior in cementitious systems incorporating this SCM. Companion pastes incorporating SF are also studied to provide comparisons between the behavior of the two high-performance SCMs. Detailed studies on non-evaporable water and calcium hydroxide contents are reported along with a model to predict the total degrees of hydration, and thus the porosity in blended pastes.

2. Experimental program

Type I Ordinary Portland Cement conforming to ASTM C 150 was used for all the cement pastes in this study. A vitreous calcium aluminosilicate (VCAS) pozzolan satisfying the requirements of ASTM C 618 and C 1240, or a dry densified silica fume (SF) conforming to ASTM C 1240 was used as the cement replacement materials. Powder X-ray Diffraction (XRD) patterns of both these materials are shown in Fig. 1. The lack of crystalline components in both these materials is evident from the diffractograms. VCAS shows an amorphous band in a 2θ range of 16° to 38° whereas SF shows a 0.405 nm peak (corresponding to vitreous glass) between 16° and 32°. The amorphous band corresponding to SF is more prominent.

Modified pastes were made with: (i) 6, 9, or 15% cement replaced by VCAS, and (ii) 6, or 9% cement replaced by SF. The physical and chemical properties of the binders are given in Table 1. It can be noticed that the median particle size of VCAS is smaller than that of the cement, but larger than that of SF. But SF in the dry densified form typically consists of agglomerates of sizes greater than 10 µm[14,15]. A water–cementitious materials ratio (w/cm) of 0.42 was used for all the mixtures. In addition, mortar specimens in which cement was replaced by VCAS or SF

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at the dosages mentioned above were prepared in accordance with ASTM C 311 to determine the strength activity indices.

2.1. Determination of pozzolanicity of VCAS and SF

Strength activity index (ratio of the strength of mortar containing the SCM to the strength of the plain mortar) is the most common method to evaluate the effectiveness of a pozzolan in combination with Portland cement. While ASTM C 311 stipulates the replacement of 20% cement with SCM in the mortars, the replacement material dosages used in this study were the same used for cement pastes as explained in the previous section. Strength activity indices of a mortar with 20% cement replacement by Class F fly ash (FA) were also determined to provide a comparison to the high-performance pozzolans (VCAS and SF).

The pozzolanicity of these materials was also evaluated in this study through two rapid methods that use the reduction in electrical conductivity as an indicator of pozzolanic activity. In Method 1[16], 5 g of the cement replacement material was mixed in 200 ml of saturated calcium hydroxide solution, and the electrical conductivity of the solution determined immediately as well as after 2 min. In Method 2 [17], a small amount of the SCM was added to unsaturated calcium hydroxide solution. The use of unsaturated calcium hydroxide solution was to avoid precipitation of $Ca(OH)_2$ when the replacement materials are added. Conductivity was determined immediately and after 24 h. A longer duration was used to compensate for the influence of conductivity change caused by the dissolution of alkalis from the replacement materials.

2.2. Non-evaporable water and calcium hydroxide content determination

The loss on ignition method (LOI) was used to determine the non-evaporable water contents at all selected ages of hydration. Small pieces from the plain and modified cement pastes cured in saturated limewater were pulverized and soaked in acetone to stop further hydration. The pulverized samples were heated in an oven at 105 ± 5 °C for 24 h, and then in a muffle furnace at 1050 ± 10 °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 LOI of unhydrated cement (or of the unhydrated cement and the replacement material multiplied by their respective mass fractions). The standard deviations of the measured w_n for all the pastes were in the range of 0.004 to 0.009. The calcium hydroxide (CH) contents of the chosen pastes at selected ages were determined using thermogravimetric analysis. 50–75 mg of crushed paste was heated in a thermal analysis system to 1050 °C at a rate of 10 °C/min. The mass loss corresponding to the temperature range of 420–540 °C is taken as that associated with the decomposition of CH.

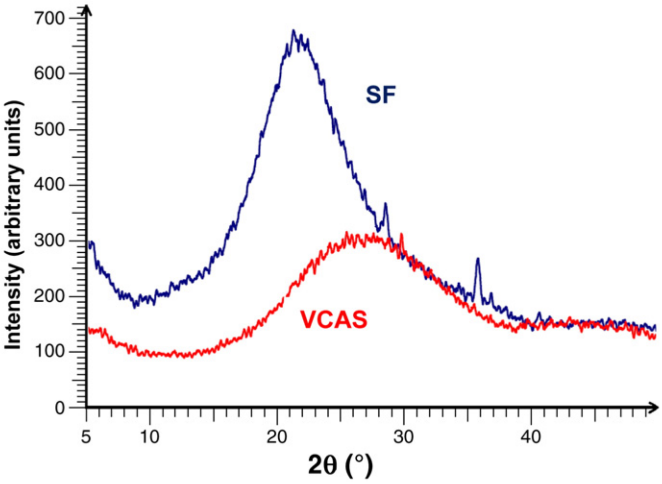

Fig. 1. XRD spectra of VCAS and SF powders.

Table 1
Chemical composition and physical properties of the binders used in this study.

Composition (% by mass)/property	Cement	VCAS	Silica fume	Fly ash
Silica (SiO_2)	20.2	54.2	93.4	50.24
Alumina (Al_2O_3)	4.7	17.8	0.42	28.78
Iron oxide (Fe_2O_3)	3.0	1.0	0.52	5.72
Calcium oxide (CaO)	61.9	24.2	1.91	5.86
Magnesium oxide (MgO)	2.6	0.8	–	1.74
Sodium oxide (Na_2O)	0.19	0.75	0.25	0.96[a]
Potassium oxide (K_2O)	0.82	0.2	0.79	
Sulfur trioxide (SO_3)	3.9	<0.1	0.34	0.51
Loss on ignition	1.9	<0.5	2.3	2.8
Median particle size (μm)	13	8	<1[b]	20
Density (kg/m^3)	3150	2600	2200	2400

[a] Equivalent alkalis.
[b] Agglomerates can be much coarser than the cement particles.

3. Results, analysis, and discussions

3.1. Ascertaining the nature of action of the replacement materials

It is well known that SF is a highly reactive pozzolanic material. For VCAS, the presence of a significant amount of CaO (Table 1) raises questions as to whether it has cementing ability or just pozzolanicity. In order to ascertain this, pastes were made by mixing VCAS powder and water at a water-to-powder ratio of 0.40. The pastes were subjected to thermogravimetric analysis (TGA) and XRD at ages of 1 and 7 days of curing. The total non-evaporable water content (water lost between 105 °C and 1000 °C) obtained from TGA was less than 0.6% for both the ages (compared to 15–20% for normal cement pastes). The thermal analysis curves also did not show any indication of the presence of CH. The XRD spectra for these pastes at both the ages were very similar to that of the raw VCAS powder, with no distinguishable crystalline peaks. Thus from TGA and XRD studies, it can be concluded that VCAS does not have any cementing effect. The pozzolanicity of both these SCMs is quantified in the following section.

3.2. Pozzolanicity of the replacement materials

The strength activity indices of cement pastes made with 6, 9, and 15% of VCAS replacing cement are shown in Fig. 2(a). The general trend from this figure is one of increasing strength activity index with increasing VCAS content. The strength activity indices are greater than 1.0 for all the mixtures, and at all times, indicating the influence of various dosages of this pozzolanic material in strength enhancement. Fig. 2(b) shows the strength activity indices of pastes modified with SF. Similar results as for VCAS are seen for SF modified pastes also. At 28 days and beyond, the paste with 9% SF replacing cement shows strength activity index values similar to that modified with 15% VCAS. For comparison purposes, the strength activity index values for a paste containing 20% Class F fly ash as cement replacement is also shown in Fig. 2(b). The better performance of VCAS and SF at both early and later ages is immediately evident from these figures.

Fig. 3 depicts the percentage reduction in conductivity determined using Method 1 and Method 2 explained earlier, which can be taken as an indicator of the pozzolanic activity of the cement replacement materials. Both methods predict higher pozzolanic activity for SF, with Method 2 bringing out the influence of SF better. When compared to the pozzolanic activity of FA, both VCAS and SF show higher

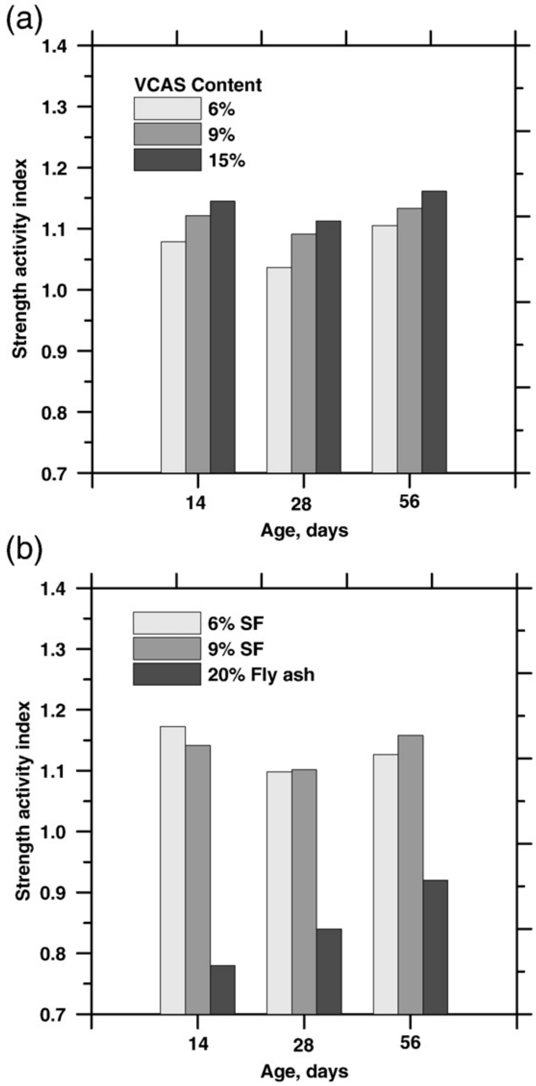

Fig. 2. Strength activity indices of: (a) VCAS modified mixtures, and (b) SF and FA modified mixtures.

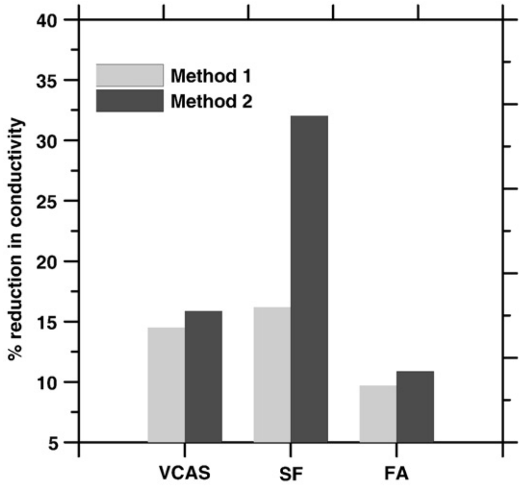

Fig. 3. Reduction in conductivity of $Ca(OH)_2$ solutions due to the addition of cement replacement materials.

pozzolanicity, which is expected based on their strength activity indices.

3.3. Non-evaporable and hydrate water contents

For plain cement pastes, non-evaporable water content (w_n) can be used to determine the degree of hydration. For pastes with SCM, extracting the degree of hydration from w_n is difficult because of the difficulties in separating the water associated with the reaction of the SCM from that of cement hydration. Since the pozzolanic reaction of the SCM typically does not bind as much water as cement hydration, and because of the presence of a lower cement content, it is obvious that the non-evaporable water content per unit mass of binder will be lower for the modified pastes at all ages[5,18–20]. The use of non-evaporable water content per unit mass of cement has been adopted in some studies, but it requires an assumption that the SCM either does not react or contribute to w_n, which is not entirely true.

The non-evaporable water contents per unit mass of binder (w_n) for pastes containing VCAS and SF are shown in Fig. 4(a) and (b) respectively. From Fig. 4(a), it can be observed that the w_n values are lower for pastes modified with VCAS as compared to the plain paste, which is expected because of the reasons stated above. Higher the VCAS content, lower the w_n value. A closer look at the data for Fig. 4(a)

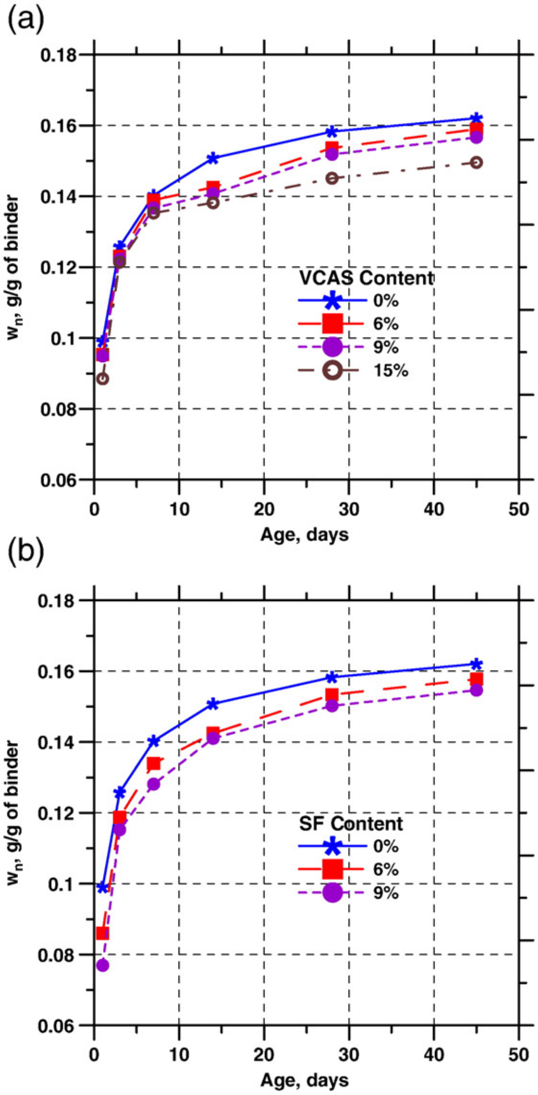

Fig. 4. Non-evaporable water contents of: (a) VCAS modified pastes, and (b) SF modified pastes.

also shows that, for all the ages, the w_n of VCAS modified pastes are greater than the w_n of the plain paste multiplied by the mass fraction of cement (m_c) in the modified paste. For instance, the w_n for 15% VCAS modified paste at 45 days is 0.15, which is greater than 0.85*0.16, where 0.16 is the w_n of plain paste. This shows that VCAS contributes to w_n by facilitating an enhancement in the hydration of available cement grains, and/or through its own pozzolanic reaction.

Fig. 4(b) shows the w_n values for SF modified pastes. Similar observations as for VCAS modified pastes are noticed in this case also. However, the w_n values for pastes with a certain SF replacement level are lower than those for pastes with the same VCAS replacement level at all ages. This results in $(w_n)_{\text{SF-modified}} - (w_n)_{\text{plain}} m_c$ being lower for the SF modified pastes than those for the corresponding VCAS modified pastes. Such an observation could be attributed in part to the lower CH contents in the SF modified pastes at all ages (about 20% lower than the plain paste for 9% cement replacement) because the water incorporated in CH is also accounted for in the w_n calculations. Thus, a comparison of the w_n values would indicate that the VCAS modified pastes are using more water for hydration than the corresponding SF modified pastes of the same mass replacement level. Also, some studies have shown that SF reacts with CH to form secondary C–S–H gel without additional water binding[21,22]. Quantification of the change in w_n, and its effect on the degree of hydration of modified pastes are dealt with in Section 3.5.

In order to separate the non-evaporable water attributed to CH, and to provide an indication of the chemically bound water in the C–S–H phase, hydrate water content can be used. Hydrate water content is the difference between the non-evaporable water content (w_n) and the water associated with CH (w_{CH}), both of which can be obtained from the TGA curves. Fig. 5 depicts the variation of hydrate water content, w_h (g/100 g of binder), in plain, 15% VCAS, 9% SF, and 20% FA modified pastes, with time. It can be observed from Fig. 5 that, at very early times, w_h is highest for the plain paste. This could be because of the higher non-evaporable water content in the plain paste compared to the modified pastes. w_h is seen to generally increase with time. By about 7 days, both the 15% VCAS modified paste and 9% SF modified paste have similar w_h as that of the plain paste. This is an indication of the pozzolanic reaction of these materials that result in a reduction in CH content. For plain pastes, however, hydrate water content is seen to be similar at both 14 and 28 days of hydration. Even though w_n increases between 14 and 28 days for the plain paste, the CH contents are also increasing because of increased cement hydration, thus resulting in similar values of hydrate water content at both these ages. At 28 days, w_h is highest for the 9% SF modified paste, followed by the 15% VCAS modified paste, attributable to the pozzolanic reaction of these materials that result in a reduction in the CH content. The 20% FA modified paste, after trailing the plain paste for 28 days, has a similar w_h value as that of the plain paste at this age, indicating that some pozzolanic reaction has occurred, but it can be readily seen that the pozzolanic reaction is slower than those of SF and VCAS. The evolution of hydrate water content with time can be used as an index of the effectiveness of the secondary reaction of the SCM.

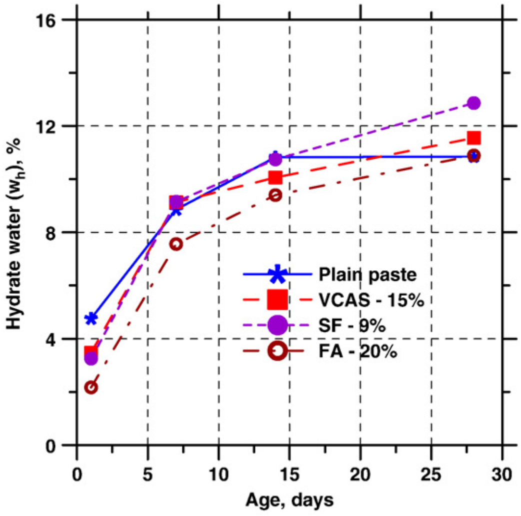

Fig. 5. Hydrate water contents of plain and modified pastes.

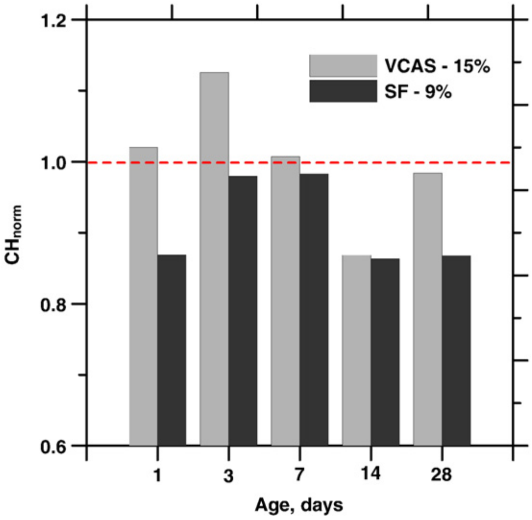

Fig. 6. CH_{norm} values of VCAS and SF modified pastes.

3.4. Calcium hydroxide contents

The CH content of the paste at any age, CH(t), can be calculated as:

$$\mathrm{CH}(t) = \frac{74.09}{18.01} \cdot \frac{m_{420}(t) - m_{540}(t)}{m_{\text{sample}}(t)} \quad (1)$$

$m_{420}(t)$ and $m_{540}(t)$ are the sample masses recorded during the TG test at 420 °C and 540 °C respectively, and m_{sample} is the anhydrous mass of the sample. The ratio (74.09/18.01) is the molar mass ratio of CH to H_2O.

CH content of plain pastes can be used as a measure of the progress of hydration. But in pastes modified with SCMs, CH(t) could be lower because of lower cement content or the pozzolanic reaction that consumes CH, or higher because of the enhancement in cement hydration in the presence of the SCM. Hence, in this paper, a normalized CH content ($\mathrm{CH}_{\text{norm}}$) is used, which is defined below.

$$\mathrm{CH}_{\text{norm}}(t) = \frac{\mathrm{CH}(t)}{\mathrm{CH}_{\text{plain}}(t) \cdot m_c} \quad (2)$$

$\mathrm{CH}_{\text{plain}}(t)$ is the CH content of the plain paste at any time t, and m_c is the mass fraction of cement in the binder. If the value of $\mathrm{CH}_{\text{norm}}$ is greater than 1.0, i.e., if $\mathrm{CH}(t) > \mathrm{CH}_{\text{plain}}(t) \cdot m_c$, it indicates that the presence of the replacement material has resulted in more CH than a plain paste with the same amount of cement. In other words, this is a clear indication of enhancement in cement hydration especially when the SCM used is only pozzolanic as is the case with SF and VCAS. For cementitious SCMs, a $\mathrm{CH}_{\text{norm}} > 1.0$ might indicate a combination of hydration enhancement as well as the hydration of the SCM. For $\mathrm{CH}_{\text{norm}}$ less than 1.0, the situation is less clear. The CH content of the modified paste can be lower than $\mathrm{CH}_{\text{plain}}(t) \cdot m_c$ because of any of the following reasons: (i) the replacement material has a retarding effect, (ii) pozzolanic reaction of the replacement material has depleted CH, or (iii) there is enhancement in cement hydration, but the secondary reaction is more dominant, resulting in reduced CH content. The final reason is more conceivable when highly active pozzolanic materials such as SF are used as SCMs. It has been reported that SF enhances cement hydration[1,20,22], and depresses the CH content because of the pozzolanic reaction even at very early ages[5,20,23].

Fig. 6 shows the $\mathrm{CH_{norm}}$ values for the pastes with 15% VCAS and 9% SF. Until a hydration age of 7 days, the $\mathrm{CH_{norm}}$ values of the VCAS modified paste are greater than 1.0, confirming the enhancement in cement hydration facilitated by the increased surfaces provided by the finer VCAS particles that are considered to be non-reactive at this time. Beyond 7 days, $\mathrm{CH_{norm}}$ stays below 1.0, because the pozzolanic reaction of VCAS consumes CH. For the SF modified paste, $\mathrm{CH_{norm}}$ is less than 1.0 at all ages, indicating the occurrence of pozzolanic reaction even as early as 1 day. $\mathrm{CH_{norm}}$ can thus be used as an indicator of the onset of pozzolanic reaction.

3.5. Total degrees of hydration of modified pastes

The previous sections have dealt with the results of experimental investigations to determine the non-evaporable and hydrate water contents, and CH contents of plain and modified pastes. In this section, a methodology to obtain the change in non-evaporable water content because of the incorporation of SCM or fillers is detailed, and this information will be used to extract the total degrees of hydration of the modified pastes.

3.5.1. Change in non-evaporable water content due to the presence of VCAS or SF

VCAS and SF contribute to w_n as shown in Section 3.3 through enhancement of cement hydration and/or its pozzolanic reaction. In order to quantify the changes in w_n because of the presence of a cement replacement material, a simple model has previously been developed[18]. The total non-evaporable water $(w_\mathrm{n})_T$ in a paste containing a cement replacement material can be expressed as:

$$(w_\mathrm{n})_T = (w_\mathrm{n})_\mathrm{c} m_\mathrm{c} + (w_\mathrm{n})_\mathrm{r} m_\mathrm{r} \tag{3}$$

where $(w_\mathrm{n})_\mathrm{c}$ and $(w_\mathrm{n})_\mathrm{r}$ are the non-evaporable water contents attributable to the hydration of cement and the pozzolanic reaction of the replacement material respectively, and m_c and m_r are their mass fractions. Since the replacement material might facilitate an enhancement in hydration of the available cement grains, $(w_\mathrm{n})_\mathrm{c}$ can be expressed as the sum of $(w_\mathrm{n})_\mathrm{c-0}$ and $(w_\mathrm{n})_\mathrm{c-r}$ where $(w_\mathrm{n})_\mathrm{c-0}$ is the non-evaporable water content of plain cement paste, and $(w_\mathrm{n})_\mathrm{c-r}$ is the non-evaporable water content resulting from the enhancement in cement hydration. Eq. (3) can then be restated as:

$$(w_n)_T - (w_n)_\mathrm{c-0} m_\mathrm{c} = (w_n)_\mathrm{c-r} m_\mathrm{c} + (w_n)_\mathrm{r} m_\mathrm{r} = (\Delta w_\mathrm{n})_\mathrm{r} \tag{4}$$

$(\Delta w_\mathrm{n})_\mathrm{r}$ can be used to express the change in non-evaporable water content in a modified paste due to the combination of enhancement in cement hydration resulting from the presence of the replacement material, and the pozzolanic reaction or secondary hydration of the replacement material (if the replacement material is a fine filler, only the enhancement in cement hydration needs to be considered). Determination of $(\Delta w_\mathrm{n})_\mathrm{r}$ is straightforward because all the terms on the far left of Eq. (4) can be easily obtained.

Fig. 7(a) and (b) shows the variation of $(\Delta w_\mathrm{n})_\mathrm{r}$ with hydration age for VCAS and SF modified pastes respectively. From Fig. 7(a), it can be seen that $(\Delta w_\mathrm{n})_\mathrm{r}$ increases rapidly during the first 7 days of hydration for the VCAS modified pastes. Higher the VCAS dosage, higher the value of $(\Delta w_\mathrm{n})_\mathrm{r}$. This increase in $(\Delta w_\mathrm{n})_\mathrm{r}$ could be attributed to the enhancement in cement hydration caused by the presence of VCAS in the mixture. This inference is strengthened by the fact that the $\mathrm{CH_{norm}}$ values at these ages of VCAS pastes shown in Fig. 6 are greater than 1.0, which was considered to indicate enhancement in cement hydration. Between 7 and 14 days, the $(\Delta w_\mathrm{n})_\mathrm{r}$ values are found to decrease for pastes of all VCAS dosages. The effect of cement hydration enhancement might have diminished by this time (due to the reduction in surfaces caused by the depletion of VCAS because of the pozzolanic reaction), and the pozzolanic reaction at early ages not potent enough to provide the same degree of increase in $(\Delta w_\mathrm{n})_\mathrm{r}$ as provided by the cement hydration enhancement. After 14 days, $(\Delta w_\mathrm{n})_\mathrm{r}$ again increases due to the increased pozzolanic reaction of VCAS, as suggested by $\mathrm{CH_{norm}}$ values of less than 1.0. The increase in $(\Delta w_\mathrm{n})_\mathrm{r}$ after 14 days is not as marked as at early ages for two reasons—compared to cement hydration, the pozzolanic reaction of VCAS is typically slower, and it does not bind as much water as cement hydration.

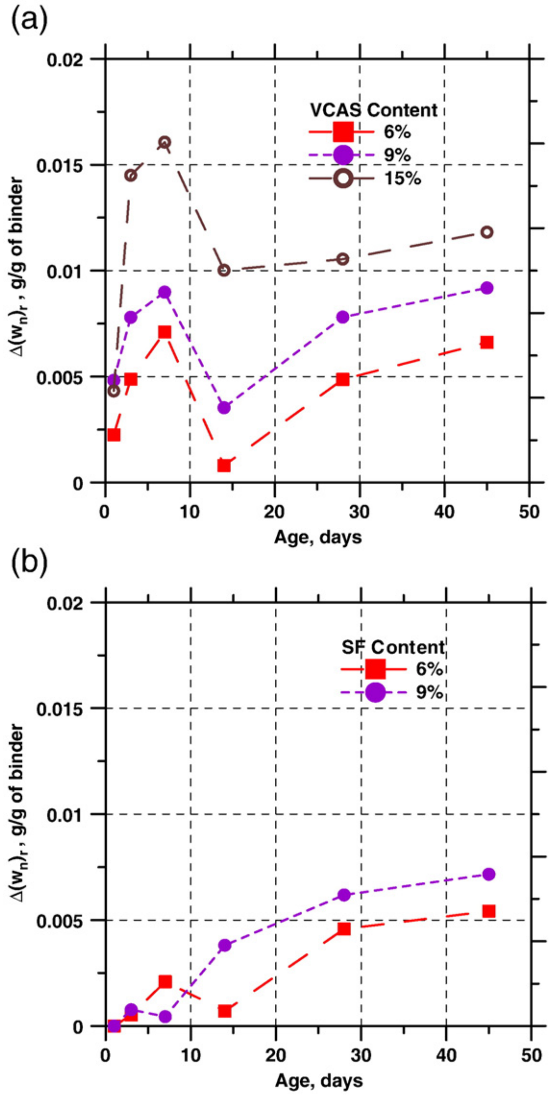

Fig. 7. Change in non-evaporable water content as result of the presence of: (a) VCAS, and (b) SF in the pastes.

The $(\Delta w_\mathrm{n})_\mathrm{r}$ values of SF modified pastes are shown in Fig. 7(b). A dominant effect of hydration enhancement is not seen at early ages as is observed for VCAS modified pastes, but SF is reacting with CH right from early ages (as seen from $\mathrm{CH_{norm}} < 1.0$). The consumption of SF early on which results in reduction of surfaces where hydration products can precipitate, and the fact that SF particles are agglomerated, results in a lack of observed hydration enhancement at early ages. It is also possible that the enhancement in cement hydration is happening in the first few hours and by the time of the first non-evaporable water content determination (after 1 day), the rate of hydration returns to a more normal level such that there is little difference between $(w_n)_{\text{SF-modified}}$ and $(w_n)_{\text{plain}} \cdot m_c$. Determination of w_n of SF modified pastes after the first few hours might show a higher $(\Delta w_n)_r$. It has been reported[24] that in SF blended pastes, CH content passes through the maxima within the first 8 h and then begins to decrease drastically. When the non-evaporable water contents reported from the experiments of[24] for a 0.45 w/cm paste with 30% SF replacement were used to determine $(\Delta w_n)_r$ based on Eq. (4), for 1 and 7 days of hydration, the values were close to zero (or lesser) similar to those reported in this study. Agglomeration of SF particles might have also resulted in the presence of some SF particles in the system even at later ages, which possibly could have facilitated some enhancement in cement hydration as compared to the plain paste. Using the non-evaporable water contents from[24], $(\Delta w_n)_r$ were calculated, and values ranging from 0.008 to 0.018 were obtained at hydration ages of 14 to 90 days. This corroborates the observations of higher later age $(\Delta w_n)_r$ also for SF modified pastes in this study.

When compared to $(\Delta w_n)_r$ of VCAS modified pastes, the values for pastes with similar SF replacements are lower, the reason for which has been explained in Section 3.3. If it is assumed that the reaction of SF with CH does not bind additional water[21,22,24], then the entire $(\Delta w_n)_r$ can be attributed to the apparent enhancement in cement hydration. This assumption will influence the prediction of the total degree of hydration as detailed below.

3.5.2. Extracting the total degrees of hydration

Since it is difficult to separate the bound water contents associated with the cement hydration and the reaction of the replacement material, quantification of the degree of hydration of blended pastes is difficult. A selective dissolution procedure[25,26], and a point-counting method[27] to determine the degrees of reaction of SCMs have been reported, but these are very involved procedures. A recent study[18] has detailed the development of a model based on mixing equation for the total degree of hydration (α_T) in pastes containing cement replacement materials.

$$\alpha_T = \frac{(w_n)_T}{(w_n)_{T-\infty}} = \left[\frac{(w_n)_c}{(w_n)_{c-\infty}}\right] m_c + \left[\frac{(w_n)_r}{(w_n)_{r-\infty}}\right] m_r \tag{5}$$

$(w_n)_{T-\infty}$, $(w_n)_{c-\infty}$, 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.

The degrees of hydration of cement and the SCM cannot be separated using this method; rather it provides the overall degree of hydration of the binder in the paste. Also, if the pozzolanic reaction of the SCM is considered not to bind any additional water (like in the case of SF), the total degree of hydration predicted by this model will be an "apparent" value that is based on the hydration of the cement in the system. Hence a total "apparent" degree of hydration $(\alpha_T)_{\text{app}}$ is used for SF modified pastes.

Since $(w_n)_c$ can be expressed as the sum of $(w_n)_{c-0}$ and $(w_n)_{c-r}$, Eq. (5) can be rewritten as:

$$\alpha_T = \left[\frac{(w_n)_{c-0}}{(w_n)_{c-\infty}}\right] m_c + \left[\frac{(w_n)_{c-r}}{(w_n)_{c-\infty}}\right] m_c + \left[\frac{(w_n)_r}{(w_n)_{r-\infty}}\right] m_r \tag{6}$$

For SF modified pastes, $(w_n)_r = 0$, if it is assumed that the formation of C–S–H from SF and CH and does not consume any additional water. Then, from Eq. (4), $(w_n)_{c-r}\, m_c = (w_n)_T - (w_n)_{c-0}\, m_c = (\Delta w_n)_r$. Using this in Eq. (6) gives:

$$(\alpha_T)_{\text{app}} = \left[\frac{(w_n)_{c-0}}{(w_n)_{c-\infty}}\right] m_c + \left[\frac{(\Delta w_n)_r}{(w_n)_{c-\infty}}\right] \tag{7}$$

The Bogue composition of the cement calculated using the oxide contents, along with the reported chemically bound water contents of the compounds[28] were used to calculate the ultimate non-evaporable water content of cement $(w_n)_{c-\infty}$, which for the cement used in this study is 0.227. All the other terms in the right hand side of Eq. (7) were easily obtained from experiments as explained earlier.

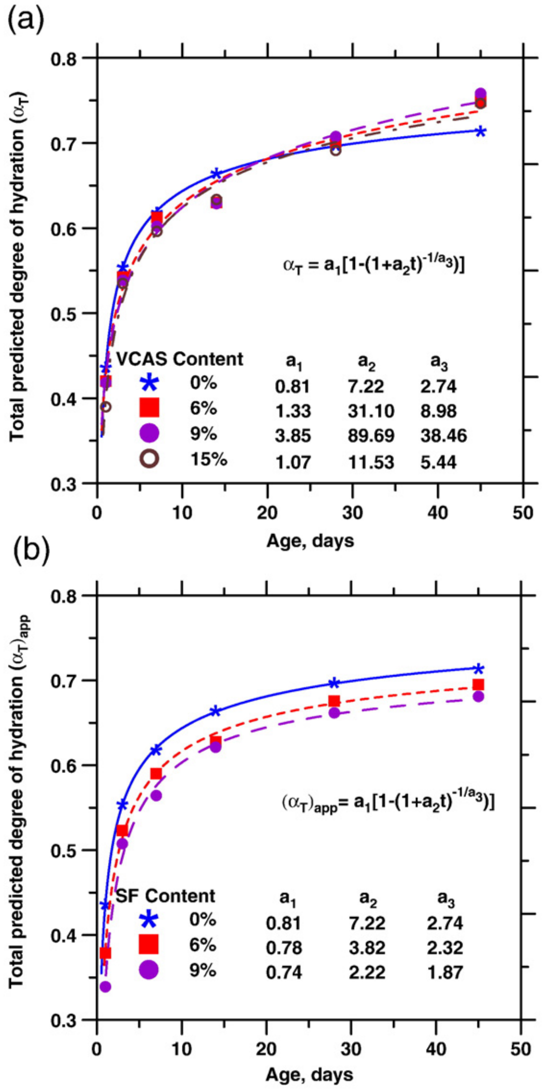

Fig. 8. Development of degrees of hydration for: (a) VCAS modified pastes, and (b) SF modified pastes.

For the VCAS modified pastes, for the first 7 days, the situation is straightforward. The rapid increase in $(\Delta w_n)_r$ values seen in Fig. 7(a) can be attributed to enhancement in cement hydration—i.e., $(w_n)_r = 0$. Thus the total degree of hydration of VCAS modified pastes until 7 days can be predicted using Eq. (7). After 7 days, it is clear that pozzolanic reaction of VCAS is occurring, based on the $(\Delta w_n)_r$ and CH_{norm} values. If it is assumed that no hydration enhancement is occurring during these times, i.e., if $(w_n)_{c-r} = 0$, then substituting $(w_n)_r\, m_r = (w_n)_T - (w_n)_{c-0}\, m_c = (\Delta w_n)_r$ from Eq. (4) into Eq. (6) gives:

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

Since the ultimate non-evaporable water contents $(w_n)_{r-\infty}$ of replacement materials are much lower compared to that of the cement (0.05 has been reported for fly ash[19], and since VCAS is pozzolanic and has similar Al_2O_3 and SiO_2 contents as that of fly ash, a value of 0.05–0.06 is assumed here for VCAS also), considering that

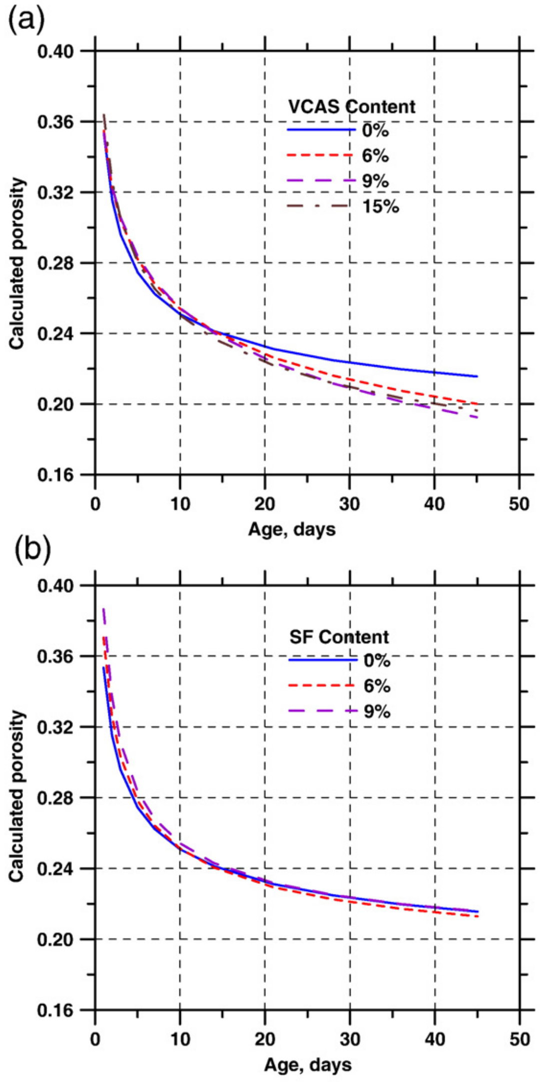

Fig. 9. Capillary porosity as a function of time for: (a) VCAS modified pastes, and (b) SF modified pastes.

the contribution towards $(\Delta w_n)_r$ is only from pozzolanic reaction leads to very high values for the second term in the right hand side of Eq. (8), and thus unrealistically high total degrees of hydration. While discussing the scenario with $CH_{norm} < 1.0$ in Section 3.4, it was stated that when highly active SCMs are used, both enhancement of cement hydration and pozzolanic reaction are possible. Hence a weighted average of α_T values from Eqs. (7) and (8) for hydration ages beyond 7 days of VCAS modified pastes is used in this study. Enhancement of cement hydration is given a higher weighting at earlier times (100% until 7 days, and linearly decreasing to 25% at 45 days) and the pozzolanic reaction is given a higher weighting at later ages (0% at 7 days, linearly increasing to 75% at 45 days).

The total degrees of hydration in VCAS and SF modified pastes determined using the procedure described above are shown in Fig. 8(a) and (b) respectively. It can be observed from Fig. 8(a) that the α_T values of VCAS modified pastes are lower than those of plain pastes at earlier times, and after about 20 days or so, the α_T values are higher, indicating the contribution from the pozzolanic reaction of VCAS. Based on the trends in this curve, it can be seen that the α_T values of VCAS modified pastes will increase further beyond 45 days, while the α_T of plain paste has essentially plateaued. For the SF modified pastes, as shown in Fig. 8 (b), the $(\alpha_T)_{app}$ values are always lower than the α_T of the plain pastes. Increasing SF contents result in decreasing values of total degrees of hydration, a trend that is reported in[29,30] also.

The relationship between total degree of hydration and time can be adequately expressed using a modified three-parameter hyperbolic expression of the form:

$$\alpha_T = a_1\left[1 - \frac{1}{(1 + a_2 t)^{1/a_3}}\right] \tag{9}$$

where a_1, a_2, and a_3 are fitting parameters, the values of which are shown in the respective figures. The continuous lines in Fig. 8(a) and (b) represent the fits of Eq. (9) to the calculated total degrees of hydration. This equation is found to predict the total degrees of hydration of the plain and modified pastes with an R^2 value greater than 0.98 in all cases.

3.6. Porosity of plain and modified pastes

The use of Mercury Intrusion Porosimetry (MIP) to determine the porosities of cement pastes is quite common. However, in this study, the capillary porosities of the plain and modified pastes at all ages, $\phi(t)$, were determined using an expression based on Power's model for hydration[31]:

$$\phi(t) = \frac{\rho_{binder} \cdot (w/cm) - f_{exp} \cdot \alpha_T(t)}{1 + \rho_{binder} \cdot (w/cm)} \tag{10}$$

where ρ_{binder} is the specific gravity of the binder in the paste (obtained from the specific gravities of cement and replacement material by accounting for the mass fraction of the constituents in the paste), and f_{exp} is the volumetric expansion coefficient for the hydration products relative to the binding materials reacted (taken as $2.15 - 1 = 1.15$, assuming that the hydration products have the same volume, plain or blended). α_T values were obtained from the three-parameter hyperbolic expression given in Eq. (9).

Fig. 9(a) and (b) depicts the variation in capillary porosity with time for VCAS and SF modified pastes respectively, as determined using Eq. (10). As can be seen from Fig. 9(a), the porosities of VCAS modified pastes are lower than that of the plain paste after about 14 days. A general reduction in porosity with increase in VCAS dosage after this age is observed, confirming the pozzolanic activity of VCAS. Thus the incorporation of VCAS can be expected to reduce the porosity in cement based materials, consequently paving the way for better material properties. From Fig. 9(b), it can be noticed that there is

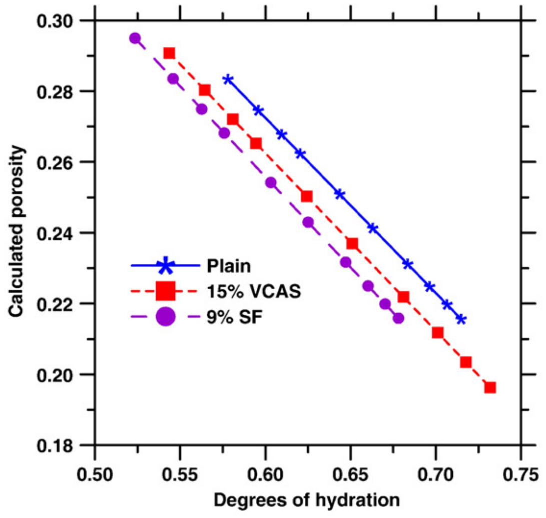

Fig. 10. Degree of hydration–porosity relationships for plain and modified pastes.

essentially no difference in the values of capillary porosity between the plain and SF modified pastes at the same w/cm. Though the porosities of SF modified and plain mixtures were found to be similar in other previous studies also[21,32–35], it is well accepted that the incorporation of SF results in pore size refinement[20,22,32,33,35]. Companion studies on concrete mixtures of same w/cm have shown that SF modified mixtures have lower sorptivity (S) and moisture diffusion coefficient (D_m) values than both the plain and VCAS modified mixtures at the same replacement level[13]. This is because fluid transport through cylindrical pores is proportional to the fourth power of the pore radius. Thus pore refinement, as in the case of SF modified mixtures, results in greatly reduced fluid transport parameters such as S and D_m. The porosities predicted using the approach for SF modified pastes described here matches closely with the porosities of similar pastes determined using MIP in[34].

However, when the porosities at equal degrees of hydration are considered, another picture emerges. Fig. 10 depicts the porosities of the plain, 15% VCAS, and 9% SF modified pastes as a function of the total degrees of hydration. The data for 3 days of hydration or more are only presented here. At equal degrees of hydration, the SF modified pastes show the lowest porosity, which has been reported in[30] also. The plain paste has the highest porosity for the same degree of hydration, followed by the VCAS modified paste.

4. Conclusions

A comprehensive study on the hydration characteristics of cement pastes modified with VCAS and SF has been reported in this paper. Non-evaporable water contents, CH contents, and a model for degree of hydration have been used to extract pertinent information about the hydration of cementitious systems incorporating these cement replacement materials, and changes in material microstructure as a result of hydration. The following conclusions were drawn from this study.

- VCAS was found to have no cementing effect; however it was found to be an effective pozzolan based on strength activity index and electrical conductivity tests. Increasing amounts of both VCAS and SF in the paste led to reduction in non-evaporable water contents (w_n) as compared to the plain paste. The VCAS modified pastes were found to use more water for hydration as compared to SF modified pastes of similar replacement level. The hydrate water content (w_h) that indicates the chemically bound water in the C–S–H phase was highest for the SF modified paste after 45 days of hydration, while the plain paste showed the lowest value.
- A normalized CH content (CH_{norm}) was defined in this paper in order to quantify the efficiency of the SCMs in reducing CH content in cement pastes, and thus its pozzolanicity. This parameter was found to be effective in determining whether the replacement material results in enhancement of cement hydration or pozzolanic reaction. SF was found to be beneficial in reducing the CH contents even at very early ages (as early as day 1), while VCAS resulted in hydration enhancement until about 7 days, and then started to reduce the CH contents in the pastes.
- An expression for the change in non-evaporable water content $(\Delta w_n)_r$ brought about by the presence of the SCM was used in order to extract the total degrees of hydration (α_T) of the pastes using a mixing model. The α_T values of VCAS modified pastes were found to be lower than those of plain pastes at earlier times, and higher at later times indicating the pozzolanic reaction of VCAS. The apparent α_T values for SF modified pastes were observed to stay lower than that of the plain paste because the pozzolanic reaction of SF was considered not to bind additional water. Published literature also points to a lower total degree of hydration in silica fume modified pastes.
- The capillary porosities calculated from the predicted degrees of hydration were lower for VCAS modified pastes than those of plain and SF modified pastes at later ages. This points to the beneficial effect of VCAS in porosity reduction, and thus in improving the properties of concrete containing this SCM. The porosities of plain and SF modified pastes were essentially the same at later ages, which is also in line with previous studies. When porosities at equal degrees of hydration were considered, the 9% SF modified paste was found to have the lowest value, followed by the 15% VCAS modified paste and the plain paste.

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