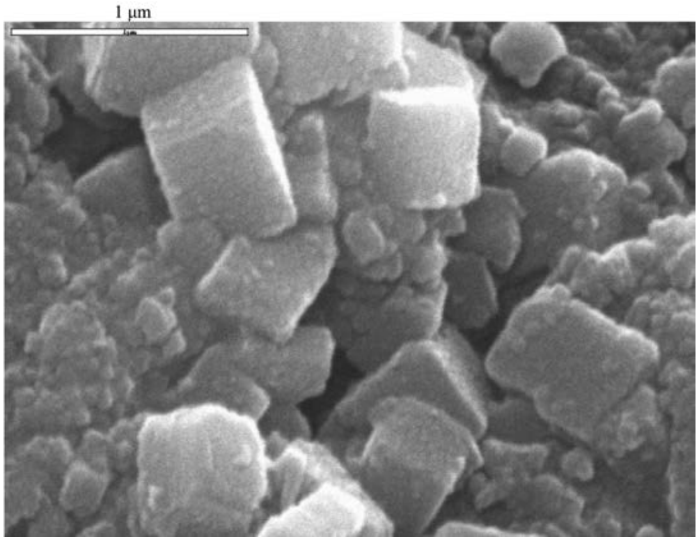

Fig. 9—Sample containing 150 nm silicon dioxide at 40,000× magnification.

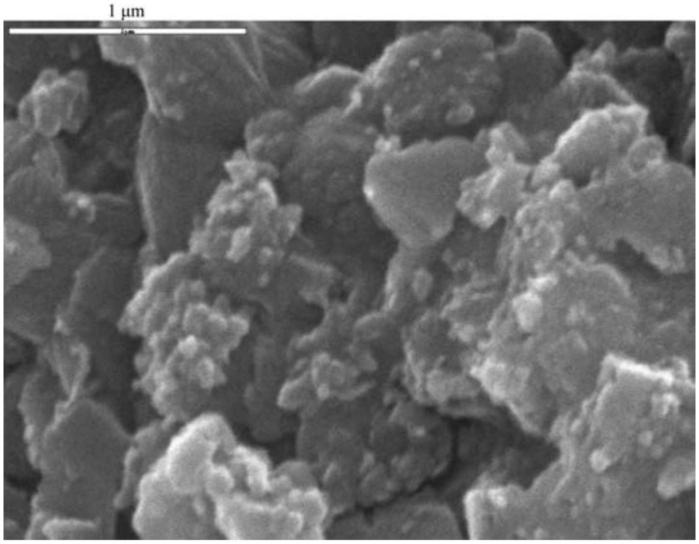

Fig. 10—Sample containing 40 nm silicon dioxide at 40,000× magnification.

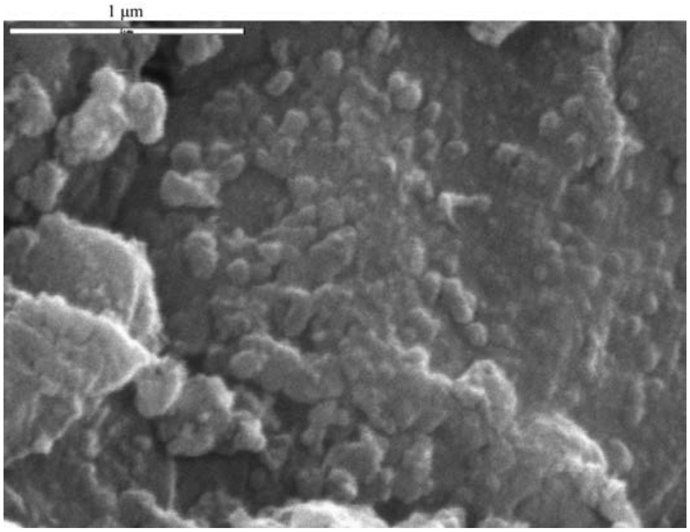

Fig. 11—Sample containing 12 nm silicon dioxide at 40,000× magnification

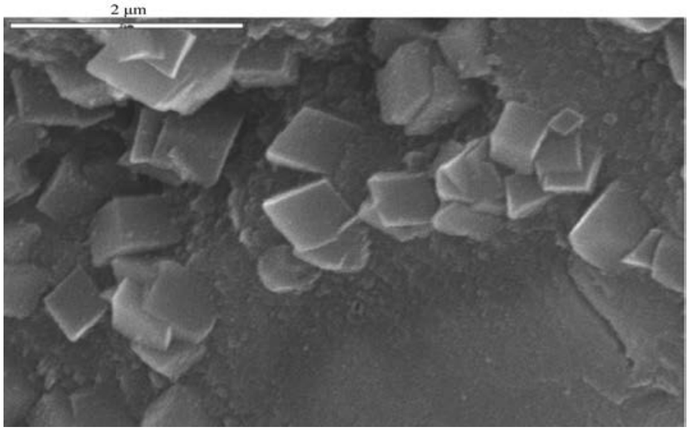

Fig. 12—Sample containing 7 nm silicon dioxide at 40,000× magnification.

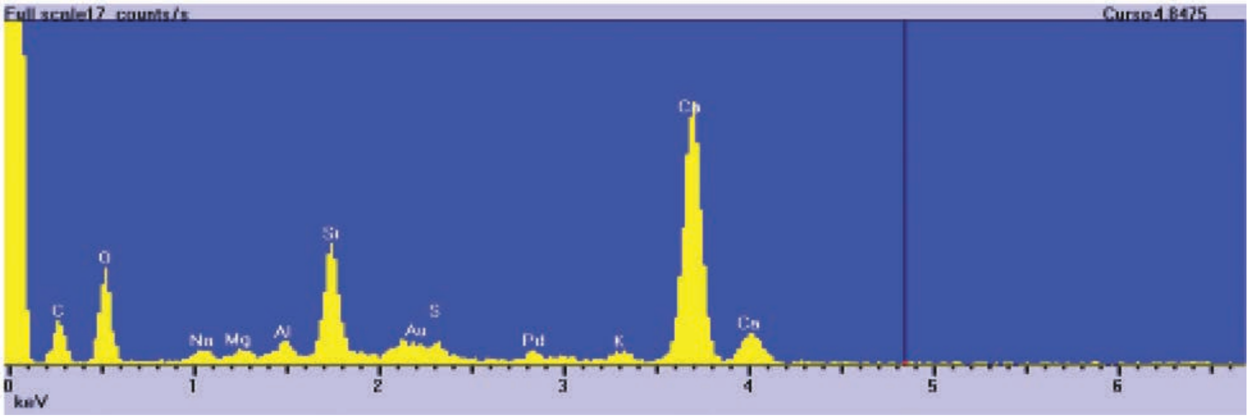

Fig. 13—EDS analysis of CSH crystals.

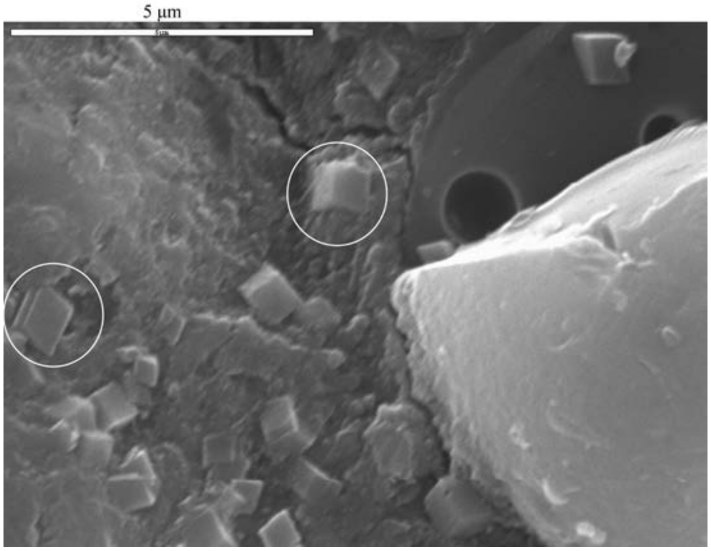

Fig. 14—Two distinct types of CSH crystals (10,000× magnification).

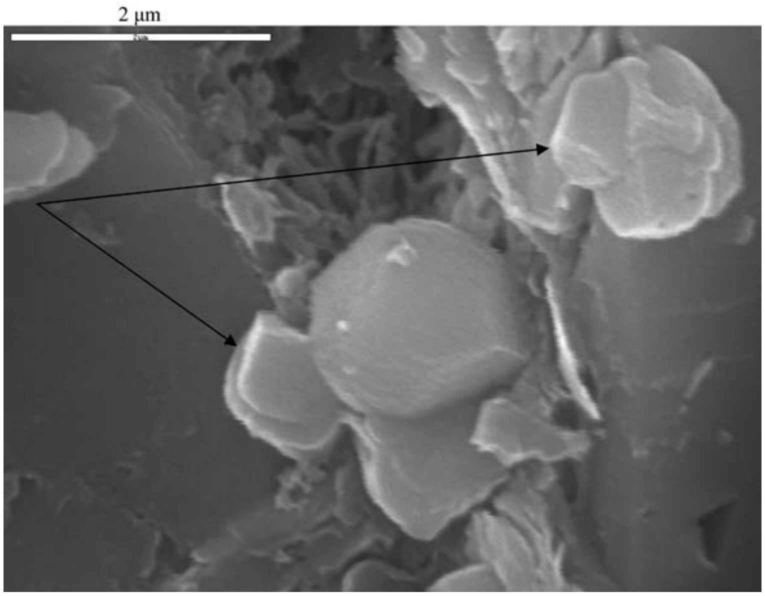

Fig. 15—Barite rosette type crystal formation (40,000× magnification).

SP-267—6

Beneficial Effects of Small Amounts of Nano-Silica on the Chemical Stability of Cement Pastes Exposed to Neutral pH Environments

by J.A. Jain and N. Neithalath

Synopsis: The effects of small dosages of nano-silica as a partial cement replacement material on the Ca ion leaching resistance of cement pastes exposed to deionized water is reported in this paper. Plain and modified cement paste specimens (containing either 6% or 9% of silica fume, or 0.5% or 1.5% of nano-silica) are subjected to leaching in deionized water for different durations after 56 days of curing in saturated limewater. The mass loss, change in porosity, and the changes in calcium hydroxide (CH) and C-S-H contents from thermogravimetric analysis between the specimens cured under saturated limewater for the entire duration and the specimens leached for different times are used to bring out the beneficial effects of these cement replacement materials when pastes are exposed to a leaching medium. The nano-silica modified cement pastes are observed to demonstrate lower mass loss and a lower increase in porosity when subjected to leaching. Using the changes in CH and C-S-H contents between the saturated and the leached pastes, it is shown that leaching and continuing cement hydration and/or pozzolanic reaction are essentially coupled, especially for the modified pastes. The paste with higher nano-silica content is seen to demonstrate increased C-S-H contents when undergoing leaching. The net Ca ion loss from both CH and C-S-H phases are seen to be lower for the pastes incorporating nano-silica as compared to those containing silica fume. The plain paste is seen to suffer the highest amount of Ca ion loss. A simplified method of calculating the apparent depth of the CH dissolution front is also reported, which is seen to highlight the influence of nano-silica and silica fume in improving the leaching resistance of pastes.

Keywords: calcium hydroxide; CH dissolution front; C-S-H; leaching; nano-silica; silica fume.

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INTRODUCTION

Leaching of calcium ions from cementitious matrices is a combined diffusion-dissolution process that results in loss of mechanical properties and long term durability issues, and can be critical for underground and underwater structures that are constantly exposed to low pH environment such as nuclear waste repositories. Pure water is one of the strong decalcifying agents for cement based materials.[1-3] The concentration gradient between the pore solution in concrete and the leachant results in diffusion of ions from the pore solution to the external leaching medium. In order to correct the imbalance caused by the diffusion of calcium ions from the pore solution into the surrounding leaching medium, calcium ions dissolve into the pore solution from the calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) phases. This dissociation of the solid phases of the cement paste results in increased porosity, and consequently loss of mechanical properties and increased permeability.[4-7]

Leaching kinetics also is significantly dependent on the initial porosity of the system.[8] Hence studies have focused on the use of supplementary cementing materials such as fly ash and silica fume that can reduce the porosity through their pozzolanic reactions, on the leaching resistance of cementitious systems.[9-11] Pozzolanic reactions also result in a reduction in the Ca-Si molar ratio of the C-S-H gel, which has also been reported to increase the leaching resistance.[12-14]

This study is aimed at assessing the influence of nano-silica as a cement replacement material on the leaching resistance of cement pastes exposed to deionized water, and to compare it with the leaching resistance of silica fume modified mixtures. The cement replacement levels of silica fume used in this study are about 10 times higher than that of nano-silica, which is in line with the difference in their particle sizes. Physical and chemical changes occurring in the system as a result of decalcification are monitored using mass loss, porosity increase, and the changes in CH and C-S-H contents. It is expected that this study will contribute to the understanding of the influence of nano-modification on the chemical stability of cement pastes in low pH conditions.

EXPERIMENTAL PROGRAM

Materials and Mixture Proportions

Type I ordinary portland cement conforming to ASTM C150 was used to prepare all the cement pastes in this study. The supplementary cementing materials used are a commercial dry densified silica fume (SF) conforming to ASTM C1240, and a commercial nano-silica (NS) obtained from Degussa Materials. The physical and chemical composition of these materials is given in Table 1. All the cement pastes were prepared using a water-cementitious materials ratio (*w/cm*) of 0.40.

The replacement of cement by silica fume was carried out at dosages of 6% and 9% by mass, whereas nano-silica was used at replacement levels of 0.5% and 1.5% by mass. The selection of dosages of silica fume was based on its commonly used dosages in construction applications. For nano-silica modified pastes, the chosen dosages were dictated by the ability to disperse nano-silica in a cement paste system. 1.5% by mass of nano-silica as cement replacement was found to be an upper threshold with respect to mixing ability of the pastes and dispersion ability. Nano-silica was dispersed in a mixture of the required mixing water and 1% of superplasticizer by mass of cement using a magnetic stirrer before adding it to the cement. The pastes were mixed in a laboratory blender and cast in specially fabricated acrylic molds (Fig. 1). The size of each specimen was 50 mm (2 in) x 50 x 3 mm (2 x 0.12 in.). The specimens were covered with a damp cloth immediately after casting, and were removed from the molds after 24 hours and cured in saturated calcium hydroxide solution (limewater) at ambient temperature (22°C [71.6°F]) for a period of 56 days. The exposure to deionized water was started after this curing duration.

Testing procedures and calculation of phase quantities before and after leaching

The specimens cured in saturated limewater for 56 days were subjected to leaching in deionized water. Prismatic specimens (50 x 50 x 3 mm [2 x 2 x 0.12 in.]) which were cured in saturated limewater were cut into sizes of 20 x 20 x 3 mm (0.78 x 0.78 x 0.12 in.) and placed separately in plastic containers filled with deionized water from which carbon dioxide was removed. The ratio of volume of leachant (deionized water) to the volume of the paste was kept as 1200. Such a high leachant to paste ratio was used to ensure that the leachant remains undersaturated in Ca ions throughout the test duration. Six specimens from each mixture were subjected to leaching while others were stored in saturated limewater for comparison.

Figure 2 shows the curing and leaching sequence for the specimens used in this study. For the set A, plain and modified paste specimens were cured in saturated limewater for 84, 112, or 146 days. The specimens in set B were cured in saturated limewater for the initial 56 days and then subjected to leaching in deionized water for a further 28, 56, or 90 days, thus making the total test duration equal to those specimens in Set A. Thus, a specimen leached for a certain duration after 56 days of curing in saturated limewater can be compared to a companion specimen stored in saturated limewater for the entire duration. For example, a specimen subjected to the regime B-2 can be compared to the one subjected to the regime A-2 to understand the influence of leaching on the material response. Typically, most studies that deal with Ca ion leaching under exposure to deionized water subject the specimens to "*x*" days of curing under saturated conditions (usually in limewater) followed by "*y*" days of leaching and compare the performance of the leached specimens that are "*x*+*y*" days old to that of saturated specimens that are "*x*" days old. In the present study, the comparisons are made between specimens that are subjected to "*x*" days of curing plus "*y*" days of leaching and "*x*+*y*" days of curing. This is expected to provide realistic indictors of the combined phenomena of leaching and continuing chemical reaction, especially in modified cement pastes.

Specimens exposed to leaching in deionized water were subjected to mass loss, porosity measurements, and thermal analysis after 28, 56, and 90 days of leaching. The leaching process followed 56 days of curing in saturated limewater. The leachant was not changed during the entire period of leaching. The specimens simultaneously stored in saturated lime water (Set A) were also subjected to thermogravimetric analysis and porosity measurements at various ages.

Porosity of unleached and leached specimens—The specimens kept in saturated lime water for 56 days and those leached in deionized water for 28, 56, and 90 days were subjected to porosity measurements as per the procedure described in [RILEM CPC11.3 1984].[15] The 20 x 20 x 3 mm (0.78 x 0.78 x 0.12 in.) size paste specimens were removed from the plastic containers, surface-dried, and kept in an oven at 105 ± 5°C (221 ± 9°F) for 24 hours to remove all evaporable water. The initial masses (m1) of the specimens were determined after cooling the specimens to the room temperature. The specimens were further subjected to vacuum for 3 hours and then saturated with water under vacuum for 1 hour, and left to soak for 18 hours. The masses (m2) were then recorded. The difference between these masses expressed as a percent of the initial volume of the specimen is reported as the porosity.

Thermogravimetric analysis on leached and unleached specimens—The unleached and leached pastes were powdered and subjected to thermogravimetric analysis (TGA) to determine the CH and C-S-H contents. TGA was carried out at the end of 56 days of curing in saturated lime water and after subsequent leaching in deionized water for 28, 56, or 90 days. The powdered sample was heated from room temperature up to 1050°C (1922°F) at a rate of 100C per minute in a Perkin Elmer TG analyzer.

The mass loss in the thermogravimetric curves between temperatures of 400 and 450°C (752 and 842°F) indicates the loss of water from CH16. The amount of CH in the specimen (as a percentage of mass of the sample at 105°C [221°F]) is calculated directly from the thermogravimetric curves using the following equation:

$$\mathrm{CH}(\%) = \mathrm{WL}_{\mathrm{CH}}(\%) \times \frac{\mathrm{MW}_{\mathrm{CH}}}{\mathrm{MW}_{\mathrm{H}}} \tag{1}$$

where $\mathrm{WL}_{\mathrm{CH}}$ corresponds to the mass loss in percentage from the TGA curve attributable to CH dehydration, and $\mathrm{MW}_{\mathrm{CH}}$ and MW_{H} are the molecular weights of CH and water respectively.

To establish the water loss from C-S-H gel, earlier studies have used mass losses corresponding to different temperature intervals between 105 and 400°C (221 and 752°F).[16-18] In this study, the mass loss between 150°C (221°F) and the temperature at which CH dehydration begins (~ 400°C [752°F]) is assumed to designate the dehydration of C-S-H gel. The quantity of C-S-H gel is calculated as:

$$\text{CSH}\ (\%) = \text{WL}_{\text{CSH}}\ (\%) \times \frac{\text{MW}_{\text{CSH}}}{2.1 * \text{MW}_{\text{H}}} \tag{2}$$

where WL_{CSH} corresponds to the mass loss in percentage that occurs during C-S-H dehydration, and MW_{CSH} and MW_H are the molecular weights of C-S-H and water respectively. Even though the commonly accepted chemical formula of C-S-H is $C_{1.7}SH_4$, some part of the four moles of water could be removed at temperatures below 150°C (221°F). The equilibrium composition of C-S-H is thus taken as $C_{1.7}SH_{2.1}$[11,16] and hence a value of 2.1 is used in the denominator of Eq. (2). This approach is applicable for plain pastes in unleached conditions. For the pastes modified with pozzolanic materials, the difference in CH contents between the plain and the modified pastes at a certain duration, adjusted by the replacement material dosage (to account for cement reduction) can be attributed to pozzolanic C-S-H formation. For every 1.1 mole of CH consumed, 1 mole of pozzolanic C-S-H ($C_{1.1}SH_{3.9}$) is produced[19] according to the relationship:

$$1.1\text{CH} + \text{S} + 2.8\text{H} \rightarrow \text{C}_{1.1}\text{SH}_{3.9} \tag{3}$$

The total mass loss that is recorded during thermal analysis is a sum of the mass loss from primary and pozzolanic C-S-H in such cases. Once the amount of pozzolanic C-S-H is determined, the amount of primary C-S-H can be determined from Eq. (2).

For pastes subjected to leaching, the calcium ion concentrations in the C-S-H phase of the leached specimens were determined based on a procedure described in Reference 11, where the increase in porosity due to leaching of C-S-H was used along with the density of CH (since even in the case of C-S-H leaching, it is actually the dissolution of CH that creates the porosity) to determine the mass loss corresponding to leaching from C-S-H. Based on the calcium ion concentration, the changes Ca-Si molar ratio in C-S-H gel due to leaching can be computed, which can then be used to determine the molecular weight of C-S-H in Eq. (2).

RESULTS AND DISCUSSIONS

Mass Loss and Changes in Porosity of Plain and Modified Cement Pastes due to Leaching

The mass losses of the plain, nano-silica and silica fume modified cement pastes due to leaching in deionized water as a percent of the initial mass of the specimen are depicted in Fig. 3. It is immediately evident from this figure that the plain paste has undergone the highest mass loss at all leaching durations. This can partly be attributed to the porous microstructure of the plain paste as compared to that of the modified pastes. The beneficial effects of microstructure modification using fine high-silica replacement materials are obvious from the relative mass losses of the plain and modified pastes. After 28 days of leaching, the 1.5% nano-silica modified paste is seen to have lost very little mass. In other words, there is relatively lesser total calcium ion loss from this paste. Even when some calcium ions would have been lost due to CH dissociation, the enhancement in cement hydration as a result of the finer particles of nano-silica and the pozzolanic reaction of nano-silica would have resulted in the creation of more CH and/or C-S-H gel, effectively negating the Ca ion loss due to leaching. At later ages, all the modified pastes are observed to lose more mass, possibly indicating the end of the dominance of pozzolanic reaction, i.e. there is no additional solid product formation. The leaching resistance, as indicated by the mass loss values, is similar for nano-silica and silica fume modified pastes at later ages. However it needs to be considered that nano-silica dosage was only a fraction of the silica fume dosage required to produce similar performance.

The porosities of the unleached and leached pastes were determined using the procedure described earlier at 28, 56, and 90 days of leaching after the initial moist curing period of 56 days. Figure 4 shows the increase in porosity of the pastes as a result of leaching in deionized water for 28, 56 and 90 days. The porosity increases when the cement pastes are exposed to deionized water because the dissolution of CH creates open porosity. Decalcification of C-S-H gel also occurs when cement pastes are subjected to leaching but the porosity created in this case is difficult to measure directly. A previous study by the authors11 has detailed an indirect methodology by which the porosity creation due to the leaching of Ca ions from CH and C-S-H phases could be separated. The plain paste shows the highest increase in porosity as compared to modified cement pastes at all ages, similar to the results from mass loss experiments.

It is known that the rate of leaching of Ca ions from CH is proportional to the initial amount of CH in the pastes20, and hence it is not surprising that the plain paste suffers the highest loss. With increase in nano-silica dosage, there is a lower change in porosity, indicating the beneficial effects of this material in increasing the leaching resistance of cement pastes. Even at later ages (longer durations of leaching), the beneficial effects of nano-silica are clearly evident. The pastes with 6% silica fume or 0.5% nano-silica as cement replacements show similar behavior at later ages. The relationship between the mass loss of all the specimens at all ages of leaching and the corresponding increase in porosity is shown in Fig. 5. A reasonable 1:1 agreement is observed between both these measured parameters (R^2 of 0.60).

Quantifying the Hydration Products in Plain and Modified Cement Pastes Before and After Leaching

Calcium hydroxide contents in leached and unleached specimens—Calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) are the two cement hydration products from which calcium ions are removed during leaching. The quantification of CH and C-S-H contents in specimens leached for 28, 56, and 90 days after initial curing in saturated lime water for 56 days and for the unleached specimens was carried out using the results from thermogravimetric analysis.

Figure 6 shows the CH contents in cement pastes stored in saturated limewater for 84, 112 and, 146 days (corresponding to Set A in Fig. 2). As expected, the CH content is the highest for the plain cement paste at all curing durations because of its higher cement content and absence of pozzolanic reactions that deplete CH. Also, CH content increases with curing duration for the plain paste. The CH content is lower for the modified cement pastes as compared to plain paste at all ages. The CH contents of the modified pastes decreases with hydration time as expected, due to the pozzolanic reactions. Higher dosages of nano-silica or silica fume are found to be more effective in reducing CH due to a contribution of consumption of CH by the highly reactive silica in these materials to form pozzolanic C-S-H gel and the reduced cement content in these pastes. The silica fume modified pastes show lower CH contents than the nano-silica modified pastes due to much higher cement replacement levels (6% and 9% of silica fume as compared to 0.5% and 1.5% of nano-silica), as well as the increased potential of nano-silica in enhancing cement hydration (and thus producing more CH) because of the increased number of surfaces it provides.

Figure 7 shows the CH contents at different ages for the plain and modified pastes stored under saturated conditions and those exposed to leaching. The first bar at each age corresponds to the CH content of the specimen cured for 56 days plus the age denoted in the X axis, in saturated limewater (corresponding to Set A in Fig. 2). The plain paste shows the highest CH content at all ages in the unleached condition, as expected. The nano-silica modified pastes show higher amounts of CH than the silica fume modified pastes, the reasons for which have been elaborated earlier. The second bar at each age corresponds to the CH content of the specimen leached for the duration shown in the X axis after being cured in saturated limewater for 56 days (corresponding to Set B in Fig. 2). The magnitude of the difference between these two bars indicates the following:

1. For the plain paste: the amounts of CH leached out and the CH produced from unhydrated cement when the specimens are subjected to a particular leaching duration, and
2. For the modified pastes: the combined effect of the amounts of CH leached out, CH consumed in pozzolanic reaction, and CH produced from the unhydrated cement, while the specimens are undergoing leaching.

For the sake of simplicity, it can be assumed that the amount of CH produced from the unhydrated cement is the same if the specimens were stored either in saturated limewater or the leachant deionized water. The extent of the pozzolanic reaction can also be assumed to be the same under both the conditions. This assumption has a limitation that, the increase in porosity created due to leaching can influence the transport of moisture into the specimen thus facilitating the hydration of hitherto unhydrated cement (producing more CH and/or C-S-H) and the pozzolanic reaction (reducing the CH and increasing the C-S-H content). For the modified pastes, the actual CH lost because of leaching might be smaller than the difference between the two bars shown in Fig. 7 for all durations because the pozzolanic reaction also consumes some CH, which cannot be considered as being leached out.

The plain paste shows the largest amount of CH loss at all durations of leaching while the pastes modified with nano-silica and silica fume show lower CH loss indicating better leaching resistance. The reason for a higher CH loss for plain paste could be its higher initial CH content, which results in an increased rate of leaching,[20] as well as its higher initial porosity as compared to the modified pastes. Microstructural densification in the modified pastes results in reduced diffusion coefficients for such pastes, providing them with increased resistance to the loss of Ca ions from CH.

It can be seen from Figure 7 that after 28 days of leaching, the nano-silica modified pastes at both replacement levels and the paste with 9% silica fume show lower difference between the CH contents in saturated and leached specimens, attributable to their denser microstructure as well as some production of additional

CH. Modified paste with 6% silica fume show similar difference in CH contents as that of plain paste at this age. While no additional CH consumption could be expected in plain paste while leaching, the difference in CH content between saturated and leached conditions for the modified pastes could also be partly due to the CH consumption by pozzolanic reaction while leaching. A certain amount of CH leaching from the exterior location of the specimen increases the diffusion coefficient, resulting in more leachant being transported to the interior of the specimen, facilitating the pozzolanic reaction. Thus the actual CH loss in the modified pastes might be lower than the difference between the bars shown in this figure, as explained earlier. The influence of combined pozzolanic reaction and leaching on the C-S-H contents of cement pastes is discussed in the next section. For longer durations of leaching, it is obvious from Figure 7 that the modified pastes suffer lesser loss of Ca ions from CH.

Calcium Silicate Hydrates (C-S-H) in leached and unleached specimens—Figure 8 shows the C-S-H contents of all the specimens as a function of their curing durations in saturated limewater. The C-S-H contents were obtained as explained in an earlier section. It can be observed from this figure that the C-S-H content increases for all the pastes with increase in curing duration. The use of both the cement replacement materials at the chosen dosages results in increased C-S-H contents as compared to the plain paste at all durations. C-S-H content is the highest for the nano-silica modified paste with 1.5% replacement level, attributable to the higher reactivity of nano-silica as compared to silica fume to form pozzolanic C-S-H gel even at much lower replacement levels, as well as the availability of more surfaces for hydration product formation. The increased C-S-H content imparts microstructural densification, which in turn reduces the porosity and provides a variety of beneficial properties for the modified pastes.

Figure 9 shows the C-S-H contents in the unleached and leached specimens at all durations, similar to the CH contents reported in Fig. 7. In addition to removal of Ca ions from CH, C-S-H also suffers the loss of Ca ions (though not to the extent of loss from CH). CH does not have to dissociate completely for C-S-H decalcification to begin 21 and this is a function of the mass (or volume) ratios of the leachant to the solid. For lower liquid-to-paste mass or volume ratios CH preferentially dissolves, while both CH and C-S-H dissociation are reported to occur in powdered samples of pastes for higher liquid-to-paste mass ratios such as 1200 used in this study.[11,21]

When the C-S-H contents of the unleached pastes and those leached in deionized water are compared, it can be seen that the plain paste loses higher amount of Ca ions from C-S-H gel. An increase in Ca ions leached from CH results in increased C-S-H decalcification to maintain equilibrium. After 28 days of leaching, there is a slight reduction in the C-S-H contents of all the modified pastes, suggesting that some Ca ions are being removed from the C-S-H gel phase. After 56 days of leaching, all the modified pastes show higher C-S-H contents compared to the specimens stored for the entire duration in saturated limewater, with the highest increase for the paste modified with 1.5% nano-silica, followed by the pastes modified with 0.5% nano-silica, 9% silica fume, and 6% silica fume. This indicates the coupling of leaching and cement hydration/pozzolanic reaction where unhydrated cement particles hydrate in the presence of the moisture that diffuses into the paste, and/or unreacted particles of nano-silica or silica fume react with CH in the presence of moisture that is diffusing into the microstructure. The beneficial effect of nano-silica as compared to silica fume even at a fraction of the silica fume dosage is very evident in this case also.

However, after 90 days of leaching, there is a net reduction in the C-S-H content for all the modified pastes. At this leaching duration, it is believed that the pozzolanic reaction or additional cement hydration that produces more C-S-H gel is complete, and the removal of Ca ions from the microstructure by the leachant dominates. Comparing the nano-silica and silica fume modified pastes, it can be seen that the reduction in C-S-H gel (the difference between the bars at a certain age in Fig. 9) is lower for the nano-silica modified pastes, i.e. these pastes are more resistant to leaching than the silica fume modified pastes. Apart from the pozzolanic reaction of nano-silica that reduces the porosity, it has been shown that that nano-silica modifies the internal structure of the C-S-H gel by increasing the average length of silicate chains, which increases calcium stabilization.[13] The net reduction in the C-S-H contents is lower for the modified pastes as compared to the plain paste. The C-S-H gel formed during pozzolanic reaction typically has a Ca-Si molar ratio of 1.1 as opposed to 1.7 for the primary C-S-H gel. While the equilibrium Ca ion concentration in the pore solution is 22 mmol/l for a Ca-Si molar ratio of 1.7 in the C-S-H gel22 (for the plain paste), this value reduces with decrease in the Ca-Si molar ratio. Hence C-S-H gel will not dissociate until the Ca ion concentration drops to a lower value in pastes of lower Ca-Si molar ratio. Thus C-S-H gels with reduced Ca-Si molar ratios such as those formed from pozzolanic reaction are much more stable than the primary gel, resulting in reduced amount of Ca ions lost from the C-S-H gel for the modified pastes.

Coupling of leaching and continuing hydration in modified cement pastes—It was shown in the previous section that the C-S-H contents for the modified cement pastes after 56 days of leaching is higher when compared to that