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In the present study the influence of three alkali cations, namely lithium, potassium and sodium, on the hydration rates and the developing capillary pore structures of hydrating cement pastes was investigated. A quantitative examination of these effects was obtained by applying a set of experimental techniques that included isothermal calorimetry, loss-on-ignition measurements and low temperature calorimetry. Low temperature calorimetry was used specifically to assess the percolation (connectivity) of pore networks with various size entryways. Differences amongst the influences of the alkalis are highlighted and discussed in terms of their intrinsic atomic characteristics.

Introduction

Alkalis, mainly potassium and sodium, are present in all Portland cements, and many specifications place limits on the allowable total equivalent alkali content. The influences of potassium and sodium on cement hydration, microstructure and performance properties has thus been a subject of considerable research for many years.^{1–6} In general, these alkalis accelerate early age cement hydration but reduce later age hydration and strength development. In recent years, numerous investigations have been performed on the addition of lithium-containing admixtures to cement-based materials, mainly as a means of mitigating the deleterious expansive cracking that occurs during alkali–silica reactions.^{7–9} These three alkali cations are each readily soluble in water and are easily incorporated into the cement hydration products.⁷ In particular, they modify the morphology of the calcium silicate hydrate (C–S–H) gel^{1,3,10} and thus the geometric and percolation characteristics of the capillary pore network.¹¹ This study examined the influences of four different sets of alkali compounds on the degree of hydration and porosity percolation.

Experimental

Cement pastes with a water : cement mass ratio (w/c) of 0.40 were prepared by mixing Cement and Concrete

Reference Laboratory (CCRL) proficiency cement sample 140¹² with water at 20°C, using a high-speed blender. The mixing water was either distilled water or a solution of alkalis, prepared by adding the appropriate compounds (see Table 1) to distilled water and stirring with a glass rod until complete dissolution. Cement 140 is a low-alkali cement, containing only 0.093% Na₂O and 0.186% K₂O per unit mass of cement.¹² Its volumetric phase composition (in terms of the four major clinker phases) as measured by scanning electron microscopy/X-ray image analysis is: 68.7% tricalcium silicate, 16.1% dicalcium silicate, 8.1% tricalcium aluminate, and 7.1% tetracalcium aluminoferrite. The additional alkalis prepared for each mixture are listed in Table 1; their masses were selected to provide the same number of moles of additional cations in each

Table 1. Mixture proportions of the cement pastes prepared in the current study

Material	No added alkalis	Alkali sulphates	Alkali hydroxides	LiOH	LiNO ₃
Cement	300 g	300 g	300 g	300 g	300 g
Water	120 g	120 g	120 g	120 g	120 g
K ₂ SO ₄		2.79 g			
Na ₂ SO ₄		2.28 g			
KOH*			2.02 g		
NaOH			1.30 g		
LiOH.H ₂ O				2.7 g	
LiNO ₃					4.42 g

*Purity of 89% as supplied by chemical company (bulk of impurity is due to presence of extra water and not K₂CO₃ which is less than 0.25%).

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mixture. The various alkali compounds in Table 1 were all readily soluble in the distilled water; the solubility of the LiOH, in particular, in a higher pH solution was verified by filtering 10 ml of pore solution from a 1 h-old $w/c = 0.4$ cement 140 paste and then dissolving the same concentration of LiOH as used in Table 1 into the extracted pore solution. After mixing, cast cylindrical wafers (approximately 5 g) of the paste were placed in sealed plastic vials. A small quantity of lime-saturated water was added to the top of the wafers to maintain saturated curing conditions. The capped vials were placed in a walk-in environmental chamber maintained at 20°C. At various ages, specimens of the pastes were removed from the vials for further analysis.

Isothermal calorimetry using a differential scanning calorimeter was conducted over the course of 24 h for a separately prepared paste of each of the five mixtures in Table 1. For the isothermal calorimetry mixtures, mixture proportions were reduced to 10 g of cement and 4 g of water (with the appropriate additions of alkalis per gram of cement to match the levels in Table 1) and mixing was conducted in a small glass beaker using a metal spatula. After mixing, 100 to 150 mg of each paste was placed in a sealed stainless steel pan that was then placed in the calorimeter cell. By requesting an isothermal scan for 24 h at 19°C, an average temperature of 20.3°C with a maximum standard deviation of 0.03°C was achieved over the course of a typical 24 h run.

Degrees of hydration of the cement pastes were further assessed using loss-on-ignition (LOI) analysis to measure the non-evaporable water content, w_n , as that quantity removed from the specimens between 105 and 1000°C, corrected for the LOI of the initial cement powder.¹³ Previously, the expanded uncertainty in the calculated w_n had been estimated to be 0.001 g/g cement.¹³ These w_n values were converted to estimated degrees of hydration based on the phase composition of the cement and published coefficients for the non-evaporable water contents of the hydrated cement clinker phases.¹⁴ Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration was 0.004.

Small pieces of the hydrated cement pastes were also utilised in low-temperature calorimetry (LTC) experiments. The sample mass was typically between 30 and 90 mg. For each LTC experiment, one small piece of the relevant cement paste was placed in a small open stainless steel pan. The pan with the sample, along with an empty reference pan of similar mass to the empty sample pan, was placed in the calorimeter cell. Using a protocol developed previously,¹⁵ a freezing scan was conducted between 5 and -55°C at a scan rate of -0.5°C/min. For temperatures between -100 and 500°C, the differential scanning calorimetry manufacturer has specified a constant calorimetric sensitivity of $\pm 2.5\%$, with a root mean square baseline noise of 1.5 μ W. The peaks observed in a plot of heat flow

versus temperature correspond to water freezing in pores with various size entryways (pore necks). The smaller the pore entryway, the more the freezing peak is depressed. Thus, a larger isolated water-filled pore will not freeze until the water in the smaller entryway pores surrounding it first freezes. The presence of, absence of, or change in peaks can be used to infer critical information concerning the characteristic sizes of the 'percolated' (connected) water-filled pores in the microstructure of the hydrating cement pastes. One advantage of the LTC over mercury intrusion porosimetry and other techniques for assessing pore size and connectivity is that the specimens may be evaluated without any drying that might damage the pore structure. However, LTC studies with variable alkali contents are complicated by the change in freezing point depression due to the variable ionic concentration of the (freezing) pore solution. For these experiments, the initial dosages of added alkalis in the cement paste mixtures would be expected to depress the freezing point of bulk water between about 1 and 3°C.¹⁶ As the alkali concentration of the pore solution becomes more concentrated during continuing hydration, this freezing point could be further depressed.

Results and discussion

Isothermal calorimetry

The isothermal calorimetry results for the five different pastes are presented in Fig. 1. In the figure, it is clear that the addition of any of the four alkali mixtures resulted in an acceleration of the early cement hydration, as the primary hydration peak was shifted to an earlier time and also generally increased in magnitude. These measurements are quite consistent with previous ones concerning the addition of NaOH to cement pastes with $w/c = 0.40$ or 0.55 ,⁶ and $w/c = 0.45$.⁴

Loss-on-ignition

As the isothermal calorimeter employed in this study has insufficient sensitivity and baseline stability for use

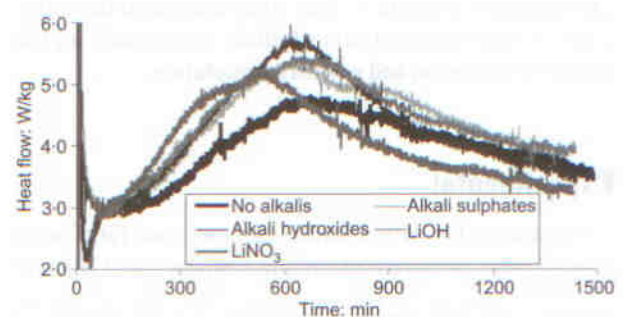


Fig. 1. Isothermal calorimetry measurements on hydrating cement pastes with various alkali additions, all with $w/c = 0.40$

beyond 24 h, LOI measurements were performed to quantify the continuing hydration in the cement pastes. The results are summarised in Table 2 which indicates the achieved degrees of hydration of the mixtures as a function of age from 1 to 91 days. Consistent with the isothermal calorimetry results presented in Fig. 1, all four of the mixtures with additional alkalis accelerated the achieved hydration during the first 3 days. However, beyond 7 days, significant differences were observed, as the alkali sulphate mixture was observed to strongly reduce the achieved hydration, the alkali hydroxide mixture was observed to generally somewhat reduce the achieved hydration, and the LiOH and LiNO₃ additions were observed to maintain a degree of hydration basically equivalent to that of the low-alkali cement control specimen.

Low-temperature calorimetry

When considering the LTC scans for the various cement pastes, three major peaks were observed, corresponding to water in (percolated) capillary pores freezing at about -15°C, water in open gel pores freezing at about -25°C, and water in dense gel pores freezing between -40 and -45°C, respectively, employing the naming convention of Snyder and Bentz.¹⁵ Previously, it has been indicated that LTC can be used to assess the percolation (connectivity) state of the capillary pore network in a hydrating cement paste.^{11,15} The presence or absence of a peak in the LTC scan near -15°C indicates a percolated or de-percolated capillary pore network, respectively. As Powers first indicated,¹⁷ as a cement paste hydrates, its capillary pores can become disconnected. The point at which this occurs will depend on the paste w/c, with pastes with a lower w/c requiring less hydration to achieve de-percolation. For a paste with a w/c of 0.40, Powers estimated that 3 days of saturated curing would be required to disconnect the capillary pores.¹⁷ Here, the influence of the various alkali additions on this percolation was examined via LTC.

Table 2. Measured degrees of hydration (via LOI) for each mixture as a function of time

Hydration time: days	No added alkalis	Alkali sulphates	Alkali hydroxides	LiOH	LiNO ₃
1	0.266	0.330	0.343	0.327	0.349
2				0.499	0.472
3	0.494	0.547	0.599		
7	0.650	0.614	0.610	0.664	0.686
8	0.659	0.644	0.661	0.692	0.699
8*	0.667	0.631			
14	0.732	0.655	0.698	0.736	0.736
30	0.764	0.671	0.738	0.761	0.764
63	0.820	0.737	0.815	0.812	0.804
91	0.846	0.762		0.831	0.834

*Replicate measurements on a separately prepared mixture.

Figure 2 provides the LTC scans obtained on saturated cement pastes of the five mixtures, cured for 2 days. At this early age, each paste still contained a highly percolated capillary pore network, as indicated by the large peaks near -15°C for each mixture (note that the ordinate scale in Fig. 2 extends from 0 to 0.10, as opposed to from 0.005 to 0.03 in Figs 3 to 7 that follow). Each paste also contained a small peak in the -40 to -45°C range, corresponding to the formation of an early age C-S-H gel containing or surrounded by dense gel pores.¹⁵ In general, the capillary pore peaks were smaller and the dense gel pore peaks were larger for the four mixtures with the additional alkalis, indicating an enhanced production of C-S-H gel and a concurrent reduction in capillary porosity relative to the low-alkali cement control specimen, in agreement

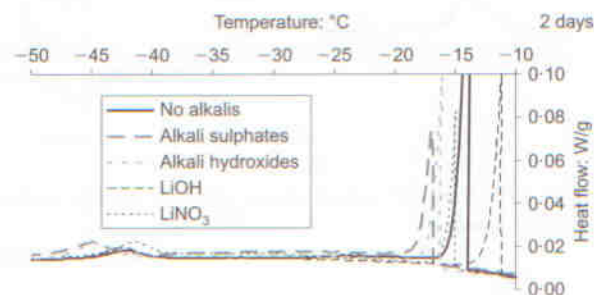


Fig. 2. LTC scans for cement pastes cured for 2 days under saturated conditions

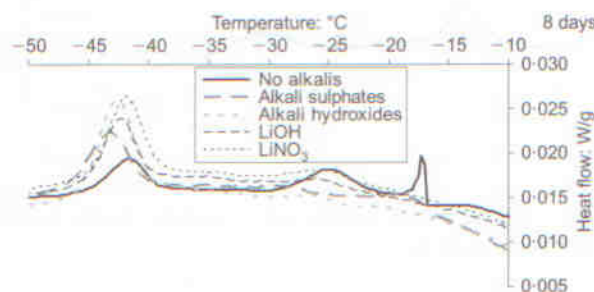


Fig. 3. LTC scans for cement pastes cured for 8 days under saturated conditions

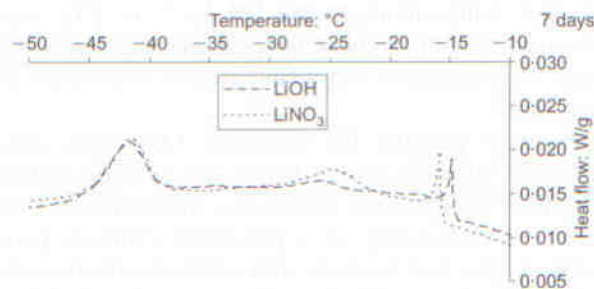


Fig. 4. LTC scans for cement pastes containing lithium after 7 days of saturated curing

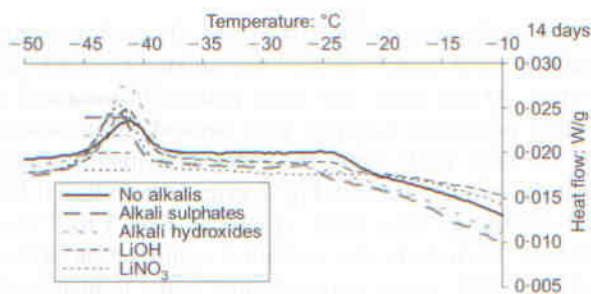


Fig. 5. LTC scans for cement pastes cured for 14 days under saturated conditions

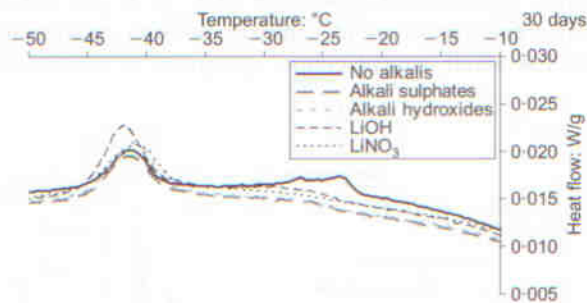


Fig. 6. LTC scans for cement pastes cured for 30 days under saturated conditions

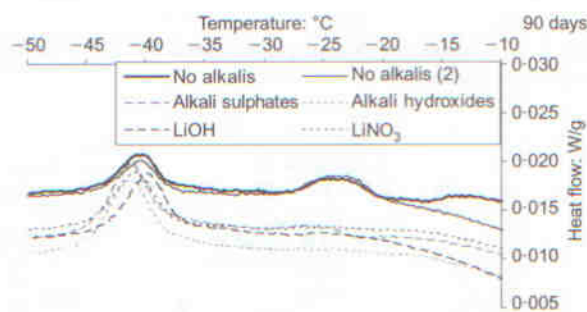


Fig. 7. LTC scans for cement pastes cured for 90 days under saturated conditions

with their higher degrees of hydration at early ages as noted in Fig. 1 and Table 2. LiOH, unlike the other three alkali additions that exhibited the expected shift of peak temperatures to the left by 1 to 3°C, was observed to shift the peak temperatures slightly to the right. No explanation is available for this observation at this time.

Figure 3 provides the equivalent LTC scans after 8 days of saturated curing. At this age, only the control low-alkali cement paste exhibited a significant peak at -15°C, corresponding to a percolated capillary pore network. The four mixtures with additional alkalis each exhibited a de-percolated capillary pore network at this age. Fig. 3 compares results for the five pastes at an equal age, and whereas the control and the pastes with

sodium and potassium additions did have essentially equal degrees of hydration (Table 2) at an age of 8 days, the two mixtures with lithium additions still had significantly higher degrees of hydration than the control after 8 days of curing. However, their degree of hydration after 7 days of curing was quite similar to those of the other three mixtures after 8 days of curing. Thus, to compare the mixtures on an equal degree of hydration basis, the 7-day LTC scans for the lithium-containing mixtures are provided in Fig. 4. Figs 3 and 4 indicate that at roughly equivalent degrees of hydration (about 0.66), the control and the two pastes with lithium additions contained percolated capillary pore networks, while the pastes with potassium and sodium additions did not.

The influence of continuing hydration on the LTC scans is provided in Figs 5, 6, and 7, which provide LTC scans obtained after 14, 30 and 90 days of saturated curing, respectively. In addition, Fig. 8 provides previously obtained LTC scans for pastes with no additional alkalis and with additional alkali sulphates after over 100 days of saturated curing.¹⁸ At 14 days, as shown in Fig. 5, each of the five mixtures exhibited a de-percolated capillary pore structure and only a little evidence of a percolated open gel pore structure. In these specimens, the presence of only a peak for the dense gel pores would generally indicate a low permeability cement paste. Normally, it would be expected that beyond this point, further saturated curing would only gradually reduce this dense gel pore peak.¹⁸ While a reduction in this peak with continuing hydration might seem counterintuitive, it must be remembered that the 'water' freezing in this peak includes not only water in dense gel pores but also that in much larger pores (open gel and capillary size) that have been de-percolated by a surrounding volume of dense gel pores. The volumes of these latter two 'size pores' would be expected to decrease with continued hydration. For sealed curing conditions, it has been observed previously that for a $w/c = 0.35$ cement paste (with 0.191% Na_2O and 0.500% K_2O per unit mass of cement), the capillary pores first de-percolate only to later re-percolate, due to autogenous stresses and

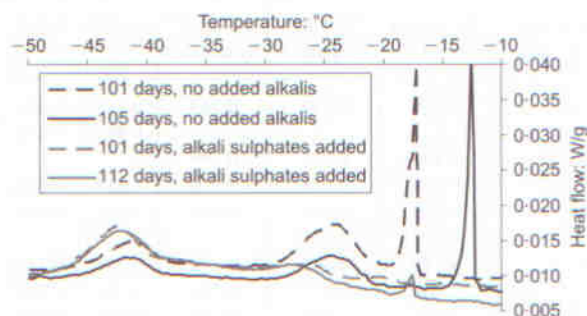


Fig. 8. LTC scans for cement pastes cured for over 100 days under saturated conditions¹⁸

strains developing in the sealed cement paste as a result of chemical shrinkage, self-desiccation, and ageing.¹⁸ Bager and Sellevold have observed a similar re-percolation of de-percolated capillary pores due to drying and re-saturation of mature cement pastes.¹⁹ Interestingly, for the low-alkali cement paste prepared in this study, this re-percolation was observed to occur even under nominally saturated conditions.

As indicated in Figs 6, 7 and 8, systems of percolated open gel and capillary pores were gradually reforming in this paste upon continued saturated curing. The paste with alkali sulphate additions also indicated some re-percolation in Fig. 8, but to a much lesser extent than that of the control low-alkali specimen. Conversely, the pastes with alkali hydroxides and the two different lithium compound additions offer no indication of re-percolation in Figs 6 and 7.

The earlier de-percolation of the pastes with additional alkalis and their enhanced stability with respect to this de-percolation are probably linked to their incorporation into the C-S-H gel hydration product and specifically their influences on its morphology and specific volume. The ionic radii of the various alkali cations, along with that of calcium, are provided in Table 3. Lithium, being the smallest of the three alkali cations, has been observed to be the alkali most preferentially incorporated into the cement hydrates.⁷ These alkalis have been observed to modify the morphology of the gel hydration product from a random to a plate-like one^{1,3} and microstructural simulations have indicated that hydration products based on plates can de-percolate the capillary pore network at a significantly lower degree of hydration than that observed for hydration products with a random morphology.¹¹ The fact that the mixtures with lithium required more hydration to achieve the initial de-percolation (at 8 days) could be rationalised by assuming that the molar volume of the C-S-H gel that incorporates the smaller lithium cation was less than that of C-S-H gel with potassium or sodium (or no) cation substitutions. A less voluminous C-S-H gel could also contribute to the strength reduction observed in systems with lithium additions.⁹

The re-percolation of the capillary pores in the low-alkali cement paste could be due to the possibility that the less crystalline, random morphology C-S-H gel^{1,3} in that paste is the most susceptible to a subsequent

rearrangement (ageing including local shrinkage) that re-percolates the capillary pore network. The old adage, 'all things in moderation', may also apply to alkali contents in cement, as a cement with too low an alkali content may produce a paste that is susceptible to re-percolation of the capillary pore network at later ages, whereas a cement with too high an alkali content may exhibit reduced hydration and strength at later ages, as well as an increased susceptibility to alkali-silica reaction. According to the results presented in this study, lithium hydroxide or lithium nitrate additions did not exhibit detrimental influences on either the long-term degree of hydration or capillary and open gel pore (re)percolation.

Conclusions

The influences of lithium, potassium, and sodium additions on the hydration rates and developing pore structure of Portland cement pastes have been presented. Although the different alkali additions exhibited some common effects, such as their acceleration of early age hydration, their influence on long-term hydration and porosity percolation was observed to be different. Lithium additions were observed to avoid both a decrease in long-term hydration and a re-percolation of the capillary pores at later ages. The differences in porosity percolation were explained based on the likely influences of alkali additions on C-S-H gel morphology and molar volume. In the low alkali cement paste prepared in this study, re-percolation of the first de-percolated capillary pore and open gel pore networks occurred due to long-term ageing effects, even under saturated curing conditions.

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Table 3. Ionic radii for various cations of relevance to this study¹⁶

Ionic species	Ionic radius: nm
Li ⁺	0.068
Na ⁺	0.097
K ⁺	0.133
Ca ⁺⁺	0.099

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