Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1645–1660

CEMENT AND CONCRETE RESEARCH

Influence of lithium-based products proposed for counteracting ASR on the chemistry of pore solution and cement hydrates

M.A. Bérubé[a,]*, C. Tremblay[b], B. Fournier[c], M.D. Thomas[d], D.B. Stokes[e]

[a]Département de géologie et de génie géologique, Université Laval, Sainte-Foy Québec, QC, Canada G1K 7P4
[b]Département de géologie et de génie géologique, Université Laval, Québec, QC, Canada G1K 7P4
[c]ICON/CANMET, Natural Resources Canada, 405 Rochester, Ottawa, ON, Canada K1A 0G1
[d]Department of Civil Engineering, University of New Brunswick, Fredericton, NB, Canada E3B 5A3
[e]FMC Lithium Division, Concrete Technology, 449 N. Cox Rd., Gastonia, NC 28054, USA

Received 8 October 2003; accepted 25 March 2004

Abstract

Low- and high-alkali cement pastes were made with or without $LiNO_3$ or a Li-bearing glass. The [Li]/[Na+K] molar ratio was kept constant to 0.74. The specimens were stored at 23, 38, and 60 °C in sealed containers. After 3, 7, 28, and 91 days, their pore solutions were extracted and analysed, and their residual water contents were obtained by drying. The Li glass was found to react quite slowly, and the corresponding $[Li^+]$ in solution progressively increased with time, temperature, fineness (as-received glass vs. ground glass), and the $[Na^++K^+]$ concentration in solution. This glass increased the pH by about 0.1, and by about 0.2 after it was finely ground. In contrast, $LiNO_3$ decreased the pH by about 0.1, despite significantly increasing the $[Na^++K^+]$ in the pore solution. The higher the total $\%Na_2O_e$ content (including Li) in the original mixtures, the higher the total alkali content incorporated in the cement hydrates. The $[Li^+]-[Na^++K^+]$ ratio in solution was about half of the initial ratio (0.74), while this ratio in the cement hydrates was always over 1.1. Li is the alkali most preferentially incorporated into the cement hydrates, while K is the least.

Keywords: Alkali–silica reaction; Alkalis; Lithium; Cement paste; Pore solution

1. Introduction

The alkali–silica reaction (ASR) is a chemical reaction between the highly basic (pH>13) and alkaline (NaOH, KOH) concrete pore solution and certain "reactive" silica mineral species inside the aggregate particles. Following this internal chemical attack, the reactive silica transforms into a silico–calco–alkaline gel that swells in the presence of water, and thus, swelling may cause expansion of the reactive aggregate particles, stresses on the surrounding cement paste, internal microcracking, expansion of the concrete element, surface macrocracking, and significant reduction of the intended service life of the structure. The extent of the reaction depends upon numerous factors; the reactivity of the aggregate to counteract, the concrete alkali content, and the moisture content and humidity conditions are the most critical. When reactive aggregates have to be used in concrete, the most popular preventive measures consist of limiting the concrete alkali content and/or using sufficient amounts of effective supplementary cementing materials (SCMs) or chemical admixtures [1].

McCoy and Caldwell [2] first observed that certain lithium-based products were capable of significantly reducing expansion due to ASR. After a limited number of studies confirmed this point during the following decades [3–5], the interest for such products resurrected in the early nineties under the SHRP program in the USA [6,7]. More recent studies also confirmed the positive effect of combining lithium compounds and fly ash [8–11]. At first, the most commonly tested lithium-based products (i.e., LiOH, LiCl, LiF, Li_2CO_3, and $LiNO_3$) seemed to produce relatively similar expansion reductions when used in concrete at similar ([Li]/[Na+K]) molar ratios [12,13]. However, a number of studies also demonstrated that insufficient dosages of LiOH, $LiCO_3$, and LiF may actually increase ASR expansion of concrete rather than reduce it, while even

---

* Corresponding author. Tel.: +1-418-656-3930; fax: +1-418-656-7339.

E-mail address: berube@ggl.ulaval.ca (M.A. Bérubé).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.03.025

increasing the pH of the concrete pore solution [7,9,14,15]. On the other hand, $LiNO_3$ appears not susceptible to such a pessimum effect [1], while not significantly increasing the pH of the concrete pore solution [15,16]. A recent study performed at CANMET (Canada) with three highly reactive aggregates also suggests that $LiNO_3$ is generally more effective against ASR than LiOH at similar molar ratios [11].

At first sight, the effectiveness of lithium for counteracting ASR is surprising, inasmuch as Li (like Na and K) is part of the alkali group in the periodic table. As mentioned before, some previous studies indicated that certain lithium salts may contribute in increasing the pH of the concrete pore solution and may even increase expansion. Lithium may also be involved in the reactions with reactive aggregates, inasmuch as it was found in the ASR gel [14,17]. According to Mo et al. [17], because of having a smaller ionic radius and a higher surface charge density, the Li^+ ions are more readily incorporated in the ASR product than Na^+ or K^+ ions, and the lithium-bearing ASR product is crystalline and nonexpansive. However, the results of Mitchell et al. [18] rather suggest that ASR is inhibited and perhaps stopped in the presence of lithium (LiOH in this case) and support the theory of the formation of a protective layer of a nonexpansive lithium-bearing silicate on the surface of the reactive aggregate particles.

Most studies performed until now indicated that the effectiveness of lithium against ASR is mainly affected by the concrete alkali content; such studies suggest that a dosage of lithium-based products corresponding to [Li]–[Na+K] molar ratios ranging between 0.6 and 1.0 is sufficient to eliminate the expansion with most reactive aggregates [1,4,9,10,12,19]. However, the effective lithium dosage may vary significantly from one reactive aggregate to another, certainly as a function of their degree of reactivity but also of their mineralogical composition. For instance, $LiNO_3$ was found to be effective with some extremely reactive aggregates, but relatively less effective with some less reactive ones [11,20]. So, the exact mechanism by which lithium can suppress ASR expansion is still not fully understood [20].

Most experimental programs performed until the early nineties involved mortar bars incorporating extremely reactive materials such as cristobalite, opal, and Pyrex. However, the tests generally performed at the time (ASTM C 227 or C 441) are more and more being considered unrealistic and/or unreliable when used for determining the effectiveness of preventive measures against ASR [21]. More recently, extensive test programs involving expansion tests on concrete specimens incorporating natural reactive aggregates have been conducted in the United Kingdom, United States, and Canada. In fact, testing concrete specimens in humid air at 38 °C and >95% RH, for instance, following the Concrete Prism Test CSA A23.2-14A or ASTM C 1293, is considered the most reliable or possibly the only reliable test method for correctly determining the effectiveness of lithium-based products against ASR. As used in Canada and the United States, this test takes 1 year to evaluate the degree of reactivity of concrete aggregates; however, the Canadian Standards Association stated that the testing period shall be extended to 2 years when testing preventive measures against ASR [1]. Such a duration is too long in many circumstances. Storing the test prisms at 60 °C rather than 38 °C may shorten the testing period, for instance, about four times, as it does when such a modification is used for testing aggregates [22]. On the other hand, the accelerated mortar bar method CSA A23.2-25A or ASTM C 1260, which takes only 2 weeks for testing both aggregate reactivity and effectiveness of SCMs against ASR, is not realistic for evaluating the effectiveness of lithium-based products. The mortar bars in this test are immersed in a 1N NaOH solution at 80 °C, which causes leaching through diffusion of the lithium initially present in the bars, thus likely reducing the beneficial effect of lithium against ASR [20]. Considering the rapidity and the great popularity of this test, some researchers proposed adding lithium to the test solution [7]. At first, such an approach appeared very interesting, but convincing results have not been obtained up to now. An important question arises about the lithium concentration of the soak solution, which, in principle, should be representative of the pore solution that prevails at equilibrium in real concrete.

2. Research significance

This study is part of an extensive research project whose objectives are (1) to evaluate the effectiveness of two lithium-based products ($LiNO_3$ and lithium-bearing glass) against a variety of Canadian reactive aggregates with different composition and reactivity, in combination or not with Canadian SCMs; (2) to determine the reaction mechanisms that could explain such an effectiveness, taking into account the nature of the reactive aggregate to counteract; and (3) to propose a rapid test method for determining this effectiveness. As part of the investigations on the reaction mechanisms, this study on cement pastes was undertaken to better assess the effect of lithium on the hydraulic system by itself (i.e., in the absence of aggregates). This is assessed as a function of the following parameters: (1) type of lithium-based product ($LiNO_3$ and Li glass); (2) concrete alkali content (low- and high-alkali cements); (3) nature and origin of the alkali load (high-alkali cement vs. low-alkali cement raised at the same alkali level by adding NaOH or KOH to the mixture water); (4) temperature; and (5) time. The principal objective is to establish the distribution of alkalis (Na, K, and Li) in the pore solution and cement hydrates as function of all the parameters mentioned above. The concrete alkali content, the origin and the nature of the alkalis, and the variation of temperature were all investigated based on the fact that all test methods used for testing the effectiveness of preventive measures against ASR, including the use of lithium-based products, are performed using temperatures (38, 60, or 80 °C) and alkali contents (NaOH addition or immersion in 1N NaOH solution) higher than in the field. The lithium-based products may behave differently as a function of these parameters. The time factor is also of importance to assess the chemical stability of the cement hydrates and of the other reaction products formed.

3. Materials and methods

3.1. Cements and lithium products

Two CSA Type-10 (ASTM Type I) cements were used: a low-alkali cement (0.51% Na_2O_e) and a high-alkali cement (1.25% Na_2O_e). The composition of the low-alkali cement is 63.6% CaO, 19.7% SiO_2, 4.74% Al_2O_3, 3.58% Fe_2O_3, 0.21% TiO_2, 1.35% MgO, 2.77% SO_3, 0.20% Na_2O, 0.47% K_2O, 3.71% LOI (loss on ignition); the composition of the high-alkali cement is 62.7% CaO, 20.5% SiO_2, 4.69% Al_2O_3, 3.23% Fe_2O_3, 0.26% TiO_2, 3.72% MgO, 3.25% SO_3, 0.43% Na_2O, 1.23% K_2O, 0.84% LOI. Two commercially available lithium-based products were used: a nitrate solution containing 30% $LiNO_3$ by mass and a Li-bearing glass, containing about 20% Li_2O by mass and with the following composition : 26.1% CaO, 50.8% SiO_2, 1.51% Al_2O_3, 0.12% Fe_2O_3, 0.20% TiO_2, 0.61 MgO,<0.1% SO_3, 0.16% Na_2O, 0.07% K_2O, 0.20% Na_2O_e 19.6% Li_2O, 0.79% LOI. The lithium glass was used both as received (14%<10 μm) and after having been finely ground (53%<10 μm).

3.2. Preparation of cement paste specimens and storage conditions

Low-alkali and high-alkali cement pastes were made with the two cements, with and without the three lithium products ($LiNO_3$ solution, as-received Li glass, and ground Li glass), always using a water–cement ratio of 0.42 (Table 1). For a number of mixtures made with the low-alkali cement, NaOH or KOH was added to the mixture water to reach 1.25% Na_2O_e by mass of cement (based on Na and K only). For all mixtures incorporating $LiNO_3$ or Li glass, the total [Li]–[Na+K] molar ratio (including cement, NaOH or KOH added, and $LiNO_3$ or Li glass) was controlled at 0.74. The paste specimens were cast into cylindrical plastic bottles (40 mm in diameter by 65 mm in length), with the bottles left opened and resting in a vertical position for 24 h over water in sealed plastic containers at 23 °C. After this initial curing period, the plastic bottles were capped; some containers remained at 23 °C, while others were stored at 38 °C (control room) or 60 °C (oven). Specimens of each mixture were subjected to all three temperatures.

3.3. Periodic measurements

At specific ages, that is, 7, 28, and 91 days after the initial curing (and also after 3 days for the specimens stored at 60 °C), paste cylinders of each mixture were

Table 1
Cement paste mixtures, storage temperature, and testing

Total % Na_2O_e[a]	0.51%	1.25% (with or without alkali addition)		
Cement (%Na_2O_e)	0.51%	0.51%	1.25%	
Alkali addition	None	NaOH	KOH	None
Control pastes	0.5% (23, 38, or 60 °C)	0.5%+NaOH (23, 38, or 60 °C)	0.5%+KOH (38 °C)	1.25% (23, 38, or 60 °C)
$LiNO_3$ (LiN) pastes[b]	0.5%+LiN (23, 38, or 60 °C)	0.5%+NaOH+LiN (23, 38, or 60 °C)	0.5%+KOH+LiN (38 °C)	1.25%+LiN (23, 38, or 60 °C)
Li glass (LiG) pastes[b]	0.5%+LiG (23, 38, or 60 °C)	0.5%+NaOH+LiG (23, 38, or 60 °C)	–	1.25%+LiG (23, 38, or 60 °C)
Ground Li glass (LiGg) pastes[b]	0.5%+LiGg (38 °C)	0.5%+NaOH+LiGg (38 °C)	–	1.25%+LiGg (38 °C)
Water–cement ratio		0.42		
Initial curing	24 h in uncapped plastic bottles maintained over water in sealed containers at 23 °C			
Storage	In capped plastic bottles maintained over water in sealed containers at 23, 38, or 60 °C			
Pore expression and analysis	After 7, 28, and 91 days for pastes stored at 23 and 38 °C; after 3, 7, 28, and 91 days for pastes stored at 60 °C			

[a] %Na_2O+0.628%K_2O, by mass of cement.
[b] [Li]–[Na+K] molar ratio=0.74.

removed from their plastic bottle, weighed (W0), and cooled at room temperature. Samples of pore solution were then expressed under high pressure (1000 MPa). The equipment used has a cylindrical chamber of 50 mm in diameter by 90 mm in length, such that the cylindrical paste specimens could be tested as is. After expression, the pore solutions were chemically analysed using inductively coupled plasma (ICP) for Na, K, and Li. Their OH^- concentrations were determined by direct titration with standardized HCl down the phenolphtalein end point, and their pH were calculated from these concentrations ($=14-\log(1/[OH^-])$). As mentioned above, all pore solutions were expressed at room temperature, and the above relationship was used for calculating their pH; however, the actual concentrations prevailing at 38 and 60 °C (for the specimens stored at these temperatures) could be a little different from those measured at 23 °C, because of the variations of all solubility products with temperature, including the dissociation product of water (pk_w). The specimens tested were also weighed after extraction (W1) to determine by difference the amount of pore solution extracted using the pore expression technique. They were then allowed to dry at 80 °C until mass equilibrium (W2). The percentage of pore water (extracted pore water+water evaporated during drying) in the original specimens were then calculated ($100\times[W0-W2]/W0$), and the percentage of the total pore solution extracted were calculated ($100\times[W0-W1]/[W0-W2]$).

3.4. Distribution of Na, K, and Li in pore solutions and cement hydrates

The total amounts of Na, K, and Li in the original specimens were calculated from the mixture proportionings (cement, water, NaOH, KOH, and lithium additions). The amounts of Na, K, and Li in the pore solution and cement hydrates (however including the unreacted lithium glass when used) were calculated from the water content of the paste specimens, assuming that the solution remaining inside the specimens after extraction, but evaporated after drying, was chemically similar to the pore solution extracted and analysed. For a better comparison between the three types of alkali involved (Na, K, and Li), all results are expressed as mol/l (pore solutions) or mol/kg (solids) of Na, K, and Li.

4. Results and discussion

4.1. Pore water contents and proportions of pore solution expressed

As expected, the pore water content tends to decrease slightly with time, due to more complete hydration, on average by about 2% between 7 and 91 days (Table 2). The amounts of pore solution extracted represent between 5% and about 25% of the total water content but are often less than 10% after 91 days. A slightly larger percentage can generally be extracted from the pastes stored at 60 °C, especially after 91 days. Inasmuch as all paste mixtures were subjected to the same load of 1000 MPa, this could likely reflect a coarser or more porous microstructure at 60 °C, then the development of a more compressible paste.

Globally, the pore water content and the proportion of extracted pore solution do not seem to be influenced by the alkali content of the system. However, the pore water content is often higher by about 1% (on a total of around 18%) in the mixtures containing lithium nitrate than in corresponding control mixtures, no matter the temperature and the time, suggesting that the presence of nitrate ions in solution slightly affects the cement hydration.

Considering the relatively low percentages of pore solution extracted, even using a load of 1000 MPa, a question may be raised about the representativity of the samples extracted. However, the pore solution that is chemically aggressive against reactive aggregates likely corresponds to the solution located in the vicinity of the aggregate particles (porous transition zone), which is possibly the solution most easily and most rapidly extracted.

4.2. pH of pore solutions

The pH in the pore solutions, computed from the OH^- concentrations, vary between 13.45 and 14.11 (Table 3). It seems to remain relatively constant with time, except perhaps at 60 °C, where a slight decrease of about 0.1 is generally observed with aging pastes. The pH also tends to be slightly less, by about 0.2, at 60 °C compared to 23 °C, for all mixtures; however, as mentioned before, the results were not corrected for temperature, with all pore solution expressions and OH^- analyses having been made at 23 °C.

On average, for the low-alkali mixtures (series 0.51%± Li), the pH is about 0.3–0.4 lower than for the high-alkali mixtures made with the same low-alkali cement but increased to 1.25% Na_2O_e (series 0.51%+NaOH±Li and 0.51%+KOH±Li), as expected. Moreover, the pH of the pore solution does not seem to be influenced by the type of alkali addition (i.e., NaOH or KOH). However, it is slightly higher (i.e., by about 0.1) for the pastes made with the high-alkali cement (series 1.25%±Li) compared to those with the same %Na_2O_e (excluding Li) but made with the low-alkali cement plus NaOH or KOH. A hypothesis is raised hereafter to explain this point.

On average, for each series of mixtures, the pH is increased by about 0.1 in the presence of the as-received Li glass and by about 0.2 in the presence of the ground glass (Table 3). It must be mentioned that the Li glass contains alkalis (0.20% Na_2O_e), which were not considered when

Table 2
Total design alkali contents, water contents, and proportions of pore solution extracted

Paste	Alkalis (mol/kg of paste)					Days	Pore water content (%)			Water extracted (% of total)		
	Na	K	Li	Total	Li/Na+K		23 °C	38 °C	60 °C	23 °C	38 °C	60 °C
0.5%	0.045	0.070	0	0.116	0	3	–	–	18.0	–	–	19
						7	18.1	18.3	18.0	20	20	18
						28	17.0	16.9	16.9	12	10	16
						91	15.8	15.8	16.0	8	9	13
0.5% +LiN[a]	0.045	0.070	0.086	0.201	0.74	3	–	–	18.5	–	–	17
						7	19.1	18.5	18.3	21	18	18
						28	18.0	17.6	17.2	12	10	12
						91	16.8	16.7	17.1	8	8	15
0.5% +LiG[b]	0.045	0.070	0.086	0.201	0.74	7	18.2	18.2	18.1	17	18	20
						28	16.8	17.0	17.1	12	16	16
						91	15.8	16.9	15.7	8	12	11
0.5% +LiGg[c]	0.045	0.070	0.086	0.201	0.74	7	–	19.0	–	18	–	–
						28	–	17.9	–	12	–	–
						91	–	17.3	–	11	–	–
0.5% +NaOH	0.214	0.070	0	0.284	0	3	–	–	18.8	–	–	20
						7	18.4	18.4	18.3	17	16	20
						28	17.9	17.8	17.4	12	11	14
						91	16.7	17.0	16.4	7	11	12
0.5% +NaOH+LiN	0.214	0.070	0.210	0.494	0.74	3	–	–	21.2	–	–	32
						7	19.8	20.1	20.7	18	18	26
						28	19.2	19.4	19.7	14	16	20
						91	18.2	17.5	19.5	8	6	19
0.5% +NaOH+LiG	0.214	0.070	0.210	0.494	0.74	3	–	–	19.0	–	–	21
						7	18.6	18.7	18.5	13	14	13
						28	18.4	17.9	17.7	12	15	20
						91	16.8	17.1	16.7	7	8	11
0.5% +NaOH+LiGg	0.214	0.070	0.210	0.494	0.74	7	–	18.7	–	–	16	–
						28	–	17.7	–	–	10	–
						91	–	16.8	–	–	9	–
0.5% +KOH	0.045	0.239	0	0.284	0	7	–	19.6	–	–	14	–
						28	–	17.8	–	–	10	–
						91	–	17.7	–	–	11	–
0.5% +KOH+LiN	0.045	0.239	0.210	0.494	0.74	7	–	19.8	–	–	14	–
						28	–	18.6	–	–	10	–
						91	–	17.9	–	–	13	–
1.25%	0.100	0.184	0	0.284	0	3	–	–	(19)[d]	–	–	–
						7	18.0	18.1	18.0	17	17	17
						28	16.8	17.1	16.1	11	8	12
						91	15.7	16.2	16.2	10	15	13
1.25% +LiN	0.100	0.184	0.210	0.494	0.74	3	–	–	(20)[d]	–	–	–
						7	18.7	18.8	19.2	17	18	19
						28	17.9	17.2	16.9	12	12	15
						91	16.7	16.5	16.9	9	12	15
1.25% +LiG	0.100	0.184	0.210	0.494	0.74	3	–	–	(18)[d]	–	–	–
						7	17.5	17.5	17.2	16	14	15
						28	17.1	16.9	16.1	10	11	10
						91	15.6	15.9	15.5	5	6	13
1.25% +LiGg	0.100	0.184	0.210	0.494	0.74	7	–	18.5	–	–	18	–
						28	–	16.8	–	–	7	–
						91	–	15.7	–	–	8	–

[a] $LiNO_3$.
[b] Bulk Li glass.
[c] Li glass ground at the cement fineness.
[d] Estimated value.

batching and that it dissolves more rapidly when it is ground, as discussed hereafter.

On the other hand, the pH is decreased by about 0.1 in the presence of $LiNO_3$ despite a higher overall $[Na^+ + K^+ + Li^+]$ concentration in the pore solution; this is surely related to the presence of nitrate ions (not analysed), which compete with the OH^- ions. The results are quite similar to those reported by Diamond [15], except that the pH was a little higher in the presence of $LiNO_3$, compared with mixtures without lithium. This author suggests that lithium added as $LiNO_3$, LiCl, or

Table 3
Chemistry of pore solutions (all concentrations and ratios are in mol/l of pore solution)

Paste	Days	23 °C					38 °C					60 °C				
		Na	K	Li	Li/Na,K	pH	Na	K	Li	Li/Na,K	pH	Na	K	Li	Li/Na,K	pH
0.5%	3	–	–	–	–	–	–	–	–	–	–	0.121	0.238	–	–	13.45
	7	0.128	0.285	–	–	13.67	0.136	0.293	–	–	13.60	0.131	0.248	–	–	13.51
	28	0.170	0.345	–	–	13.75	0.154	0.319	–	–	13.75	0.135	0.255	–	–	13.51
	91	0.160	0.329	–	–	13.76	0.142	0.302	–	–	13.45	0.135	0.261	–	–	13.45
0.5% +LiN	3	–	–	–	–	–	–	–	–	–	–	0.114	0.242	0.225	0.63	13.57
	7	0.113	0.264	0.168	0.45	13.67	0.134	0.298	0.160	0.37	13.67	0.131	0.263	0.216	0.55	13.51
	28	0.156	0.324	0.217	0.45	–	0.144	0.318	0.178	0.39	–	0.134	0.271	0.165	0.41	13.54
	91	0.137	0.300	0.198	0.45	13.58	0.148	0.334	0.196	0.41	13.76	0.128	0.269	0.206	0.52	13.58
0.5% +LiG	7	0.123	0.280	0.006	0.01	13.75	0.125	0.272	0.000	0.00	13.65	0.124	0.250	0.029	0.08	13.57
	28	0.135	0.302	0.006	0.01	–	0.130	0.278	0.010	0.02	–	0.128	0.256	0.060	0.16	–
	91	0.157	0.336	0.050	0.10	13.76	0.181	0.369	0.077	0.14	–	0.127	0.265	0.128	0.33	13.45
0.5% +LiGg	7	–	–	–	–	–	0.123	0.253	0.069	0.18	13.75	–	–	–	–	–
	28	–	–	–	–	–	0.119	0.253	0.086	0.23	13.75	–	–	–	–	–
	91	–	–	–	–	–	0.125	0.272	0.180	0.45	13.68	–	–	–	–	–
0.5% +NaOH	3	–	–	–	–	–	–	–	–	–	–	0.523	0.181	–	–	13.74
	7	0.485	0.187	–	–	13.92	0.416	0.156	–	–	13.87	0.494	0.179	–	–	13.81
	28	0.611	0.238	–	–	13.97	0.595	0.217	–	–	13.92	0.588	0.199	–	–	13.76
	91	0.603	0.247	–	–	13.93	0.589	0.224	–	–	13.82	0.566	0.198	–	–	13.76
0.5% +NaOH+LiN	3	–	–	–	–	–	–	–	–	–	–	0.655	0.232	0.429	0.48	13.78
	7	0.631	0.251	0.432	0.49	13.92	0.686	0.266	0.451	0.47	13.92	0.630	0.228	0.392	0.46	–
	28	0.693	0.278	0.399	0.41	13.87	0.743	0.286	0.433	0.42	13.80	0.716	0.259	0.397	0.41	13.69
	91	0.701	0.313	0.421	0.42	13.88	0.742	0.306	0.438	0.42	13.82	0.676	0.256	0.401	0.43	13.58
0.5% +NaOH+LiG	3	–	–	–	–	–	–	–	–	–	–	0.515	0.179	0.075	0.11	13.87
	7	0.606	0.230	0.035	0.04	14.01	0.576	0.207	0.027	0.03	13.93	0.457	0.162	0.054	0.09	13.87
	28	0.621	0.231	0.067	0.08	13.83	0.599	0.216	0.063	0.08	14.01	0.646	0.218	0.117	0.14	13.75
	91	0.577	0.234	0.110	0.14	13.98	0.591	0.225	0.131	0.16	13.93	0.590	0.209	0.234	0.29	13.82
0.5% +NaOH+LiGg	7	–	–	–	–	–	0.573	0.215	0.165	0.21	13.97	–	–	–	–	–
	28	–	–	–	–	–	0.605	0.223	0.232	0.28	–	–	–	–	–	–
	91	–	–	–	–	–	0.575	0.226	0.318	0.40	13.98	–	–	–	–	–
0.5% +KOH	7	–	–	–	–	–	0.088	0.780	–	–	13.93	–	–	–	–	–
	28	–	–	–	–	–	0.092	0.816	–	–	13.88	–	–	–	–	–
	91	–	–	–	–	–	0.100	0.790	–	–	13.93	–	–	–	–	–
0.5% +KOH+LiN	7	–	–	–	–	–	0.102	0.956	0.401	0.38	13.82	–	–	–	–	–
	28	–	–	–	–	–	0.113	1.054	0.434	0.37	13.82	–	–	–	–	–
	91	–	–	–	–	–	0.122	1.066	0.424	0.36	13.76	–	–	–	–	–
1.25%	3	–	–	–	–	–	–	–	–	–	–	0.227	0.645	–	–	–
	7	0.256	0.806	–	–	14.05	0.240	0.711	–	–	14.05	0.244	0.672	–	–	13.92
	28	0.289	0.857	–	–	14.11	0.271	0.742	–	–	14.01	0.266	0.703	–	–	13.78
	91	0.262	0.758	–	–	13.98	0.280	0.777	–	–	13.98	0.265	0.716	–	–	13.76
1.25% +LiN	3	–	–	–	–	–	–	–	–	–	–	0.301	0.870	0.430	0.37	–
	7	0.287	0.941	0.476	0.39	14.05	0.303	0.949	0.464	0.37	13.81	0.316	0.891	0.429	0.36	13.81
	28	0.300	0.935	0.409	0.33	14.01	0.319	0.929	0.439	0.35	13.92	0.342	0.918	0.393	0.31	13.71
	91	0.321	1.023	0.408	0.30	13.93	0.310	0.917	0.403	0.33	13.93	0.326	0.995	0.357	0.27	13.68
1.25% +LiG	3	–	–	–	–	–	–	–	–	–	–	0.242	0.693	0.068	0.07	–
	7	0.245	0.758	0.053	0.05	–	0.276	0.804	0.090	0.08	14.01	0.202	0.583	0.065	0.08	13.87
	28	0.268	0.787	0.063	0.06	14.08	0.287	0.778	0.076	0.07	14.05	0.259	0.700	0.107	0.11	13.83
	91	0.281	0.808	0.097	0.09	14.06	0.276	0.753	0.136	0.13	13.98	0.257	0.690	0.195	0.21	13.82
1.25% +LiGg	7	–	–	–	–	–	0.205	0.605	0.195	0.24	14.05	–	–	–	–	–
	28	–	–	–	–	–	0.292	0.792	0.254	0.23	14.08	–	–	–	–	–
	91	–	–	–	–	–	0.302	0.832	0.300	0.26	14.06	–	–	–	–	–

Li_2SO_4 would not generate LiOH in solution and would not increase the pH, in contrast with other forms such as LiF, Li_2CO_3, and LiOH.

4.3. Alkali concentrations of pore solutions

For each storage temperature, the [Na^+], [K^+], [Na^++K^+], and [Na^++K^++Li^+] of the pore solution tend to slightly increase up to 28 days, then reach a steady state (Table 3 and Figs. 1–3). Moreover, the higher the initial Na and K content in the mixtures, the higher the corresponding concentrations in the pore solution. The same trends are observed for the [Li^+] concentration for mixtures containing $LiNO_3$; this may suggest that corresponding lithium-bearing hydrates are stable with time as concerns releasing of alkali ions in the long term.

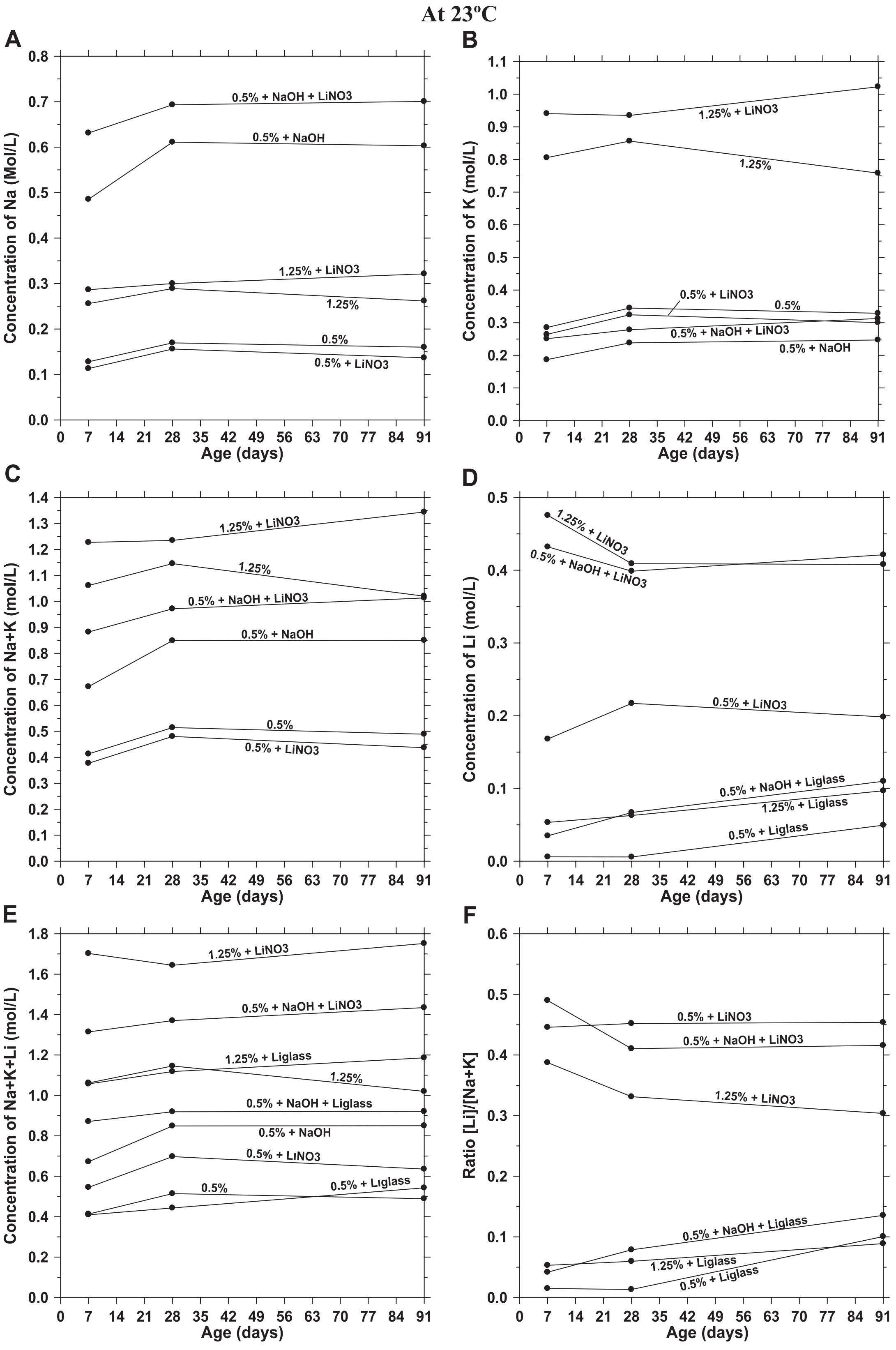

Fig. 1. Pore solution chemistry of cement pastes stored at 23 °C. (A) $[Na^+]$; (B) $[K^+]$; (C) $[Na^+ + K^+]$; (D) $[Li^+]$; (E) $[Na^+ + K^+ + Li^+]$; (F) $[Li^+]$–$[Na^+ + K^+]$. $[Na^+ + K^+]$.

However, in the presence of the Li glass, the [Li^+] concentration tends to increase slowly with time due to the progressive dissolution of the glass (Figs. 1D, 2D, and 3D).

The [Na^+] is reduced if KOH is added to the mixture water (0.5% vs. 0.5%+KOH; 0.5%+LiN vs. 0.5%+KOH+LiN; Table 3 and Fig. 2A). Interestingly, the [Na^+] in the pore solution of the high-alkali mixtures increases significantly when $LiNO_3$ is added (0.5%+KOH vs. 0.5%+KOH+LiN; 1.25% vs. 1.25%+LiN; 0.5%+NaOH vs. 0.5%+NaOH+LiN; Table 3 and Figs. 1A, 2A, and 3A). This is attributed to the fact that Li is the alkali preferentially incorporated into the cement hydrates. However, such a phenomenon was not observed in the case of the low-alkali mixtures (0.5% vs. 0.5%+LiN), which suggests in turn that the competition between the various types of alkali ions for the hydrates is less severe when the total alkali concentration is low; the hydrates are then able to accommodate each type.

The [K^+] is decreased when NaOH is added (0.5% vs. 0.5%+NaOH; 0.5%+LiN vs. 0.5%+NaOH+LiN; Figs. 1B, 2B, and 3B). As previously seen for the [Na^+], the [K^+] in the high-alkali mixtures increases significantly in the presence of $LiNO_3$ (0.5%+NaOH vs. 0.5%+NaOH+LiN; 1.25% vs. 1.25%+LiN; 0.5%+KOH vs. 0.5%+KOH+LiN; Figs. 1B, 2B, and 3B).

Figs. 1C, 2C, and 3C clearly show that the addition of $LiNO_3$ results in significantly greater [Na^++K^+] concentrations in the pore solution of the high-alkali mixtures. Interestingly, these concentrations are not the same for each of the three series of high-alkali mixtures made with similar alkali contents. For the pastes with 1.25% Na_2O_e (by mass of cement), with or without lithium addition, the highest [Na^++K^+] concentrations are obtained for the mixtures made with the high-alkali cement (1.25% Na_2O_e). This is followed by the mixtures made with the low-alkali cement (0.51% Na_2O_e) plus KOH (see Fig. 2C). The mixtures made with the same cement plus NaOH exhibited the lowest [Na^++K^+] concentrations in the pore solution. This suggests that for similar total alkali contents, alkalis added to the mixture water, all available at the early stage of cement hydration, are more completely incorporated in the cement hydrates than alkalis initially present in the cement, especially those as solid solution in C_3A and C_3S; however, the unreleased cement alkalis are progressively released with time, then enrich the pore solution and increase its pH. The results also suggest that Na is more easily incorporated into the cement hydrates than K. Consequently, the use of a high-alkali cement could be more aggressive towards reactive aggregates than a cement with a lower alkali content that is increased at the same level by adding NaOH or KOH, inasmuch as a relatively lower proportion of the total alkalis is incorporated in the hydrates, then a higher proportion remains in the pore solution.

4.4. Lithium concentrations and [Li]–[Na+K] molar ratio of pore solutions

As mentioned before, when the Li glass is used, the [Li^+] tends to slowly and progressively increase with time (Figs. 1D, 2D, and 3D). Moreover, the [Li^+] concentrations are significantly lower than those obtained for the mixtures incorporating similar molar amounts of lithium as $LiNO_3$, with a few exceptions (i.e., after 91 days at 60 °C; Fig. 3D) and at 38 °C when the glass is finely ground (Fig. 2D). For the Li glass mixtures, the fact that [Li^+] increases with time (Figs. 1D, 2D, and 3D), temperature (cf. Figs. 1D, 2D, and 3D), fineness (Fig. 2D), and [Na^++K^+] (0.5%+LiG vs. 0.5%+NaOH+LiG or 1.25%+LiG; Figs. 1D, 2D, and 3D) clearly indicates that the as-received Li glass does not release lithium rapidly, at least under normal conditions of temperature and pH. For the high-alkali mixtures incorporating $LiNO_3$, the higher the original Li content in the mixture, the higher the residual [Li^+] in the pore solution, which is not surprising. For a same Na_2O_e content of 1.25% by mass of cement in the original mixture (excluding lithium), the [Li^+] is not significantly affected by the nature of the other alkalis in the system (1.25%+LiN ≈ 0.5%+KOH+LiN ≈ 0.5%+NaOH+LiN; Figs. 1D, 2D, and 3D).

For all mixtures incorporating $LiNO_3$ or Li glass, the total [Li]–[Na+K] molar ratio was controlled at 0.74. Figs. 1F, 2F, and 3F indicate that this ratio in the pore solution is significantly less than as added. For the mixtures made with $LiNO_3$, it generally ranges between 0.30 and 0.45, whatever the temperature and the age of the specimens; in other words, only half or less of the added lithium is found in the pore solution, as observed by Diamond [15]. For the mixtures incorporating the as-received Li glass, the ratio increases progressively with time from almost 0 to about 0.15 at 23 °C or 38 °C, and from 0.05 to 0.35 at 60 °C. With the ground glass tested only at 38 °C, this ratio is higher, increasing with time from 0.15 to 0.45.

If the accelerated mortar bar test CSA A23.2-25A or ASTM C 1293 is used to evaluate the effectiveness of soluble Li salts against ASR by incorporating lithium in the test solution, the results obtained indicate that this ratio in the test solution should be adjusted with respect to the actual ratio observed at equilibrium in the pore solution of nonimmersed control specimens.

4.5. Proportions of alkalis in pore solutions and cement hydrates

The results obtained for the proportions of Na, K, Na+K, and Li in the pore solution are presented in Fig. 4 (23 °C), 5 (38 °C), and 6 (60 °C). The calculations are based on the total (design) amounts of alkalis in the original mixtures (Table 2), the pore water contents (Table 2), and the alkali concentrations in the extracted pore solutions (Table 3). The following observations are drawn regarding the control

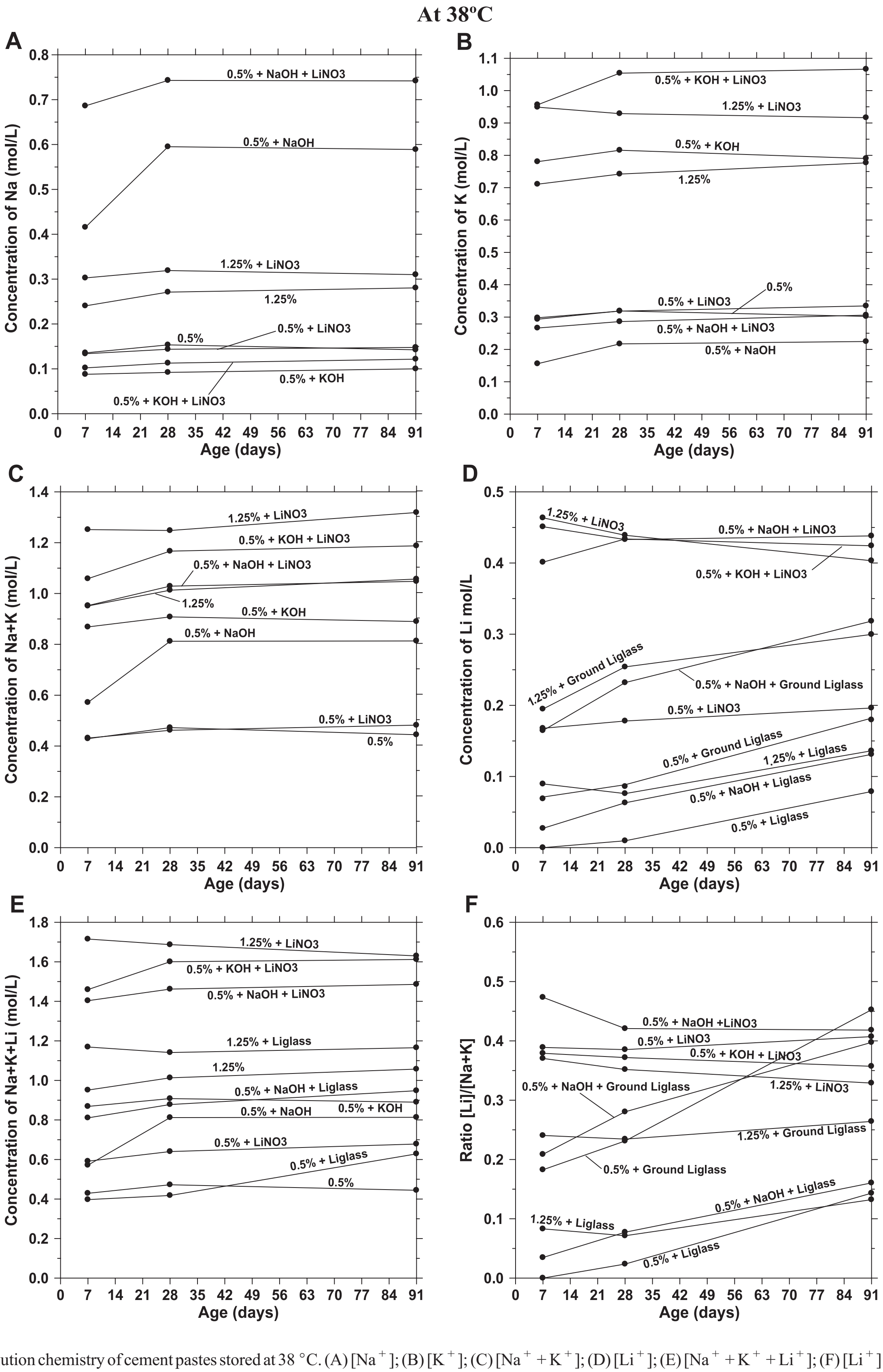

Fig. 2. Pore solution chemistry of cement pastes stored at 38 °C. (A) $[Na^+]$; (B) $[K^+]$; (C) $[Na^+ + K^+]$; (D) $[Li^+]$; (E) $[Na^+ + K^+ + Li^+]$; (F) $[Li^+]-[Na^+ + K^+]$. $[Na^+ + K^+]$.

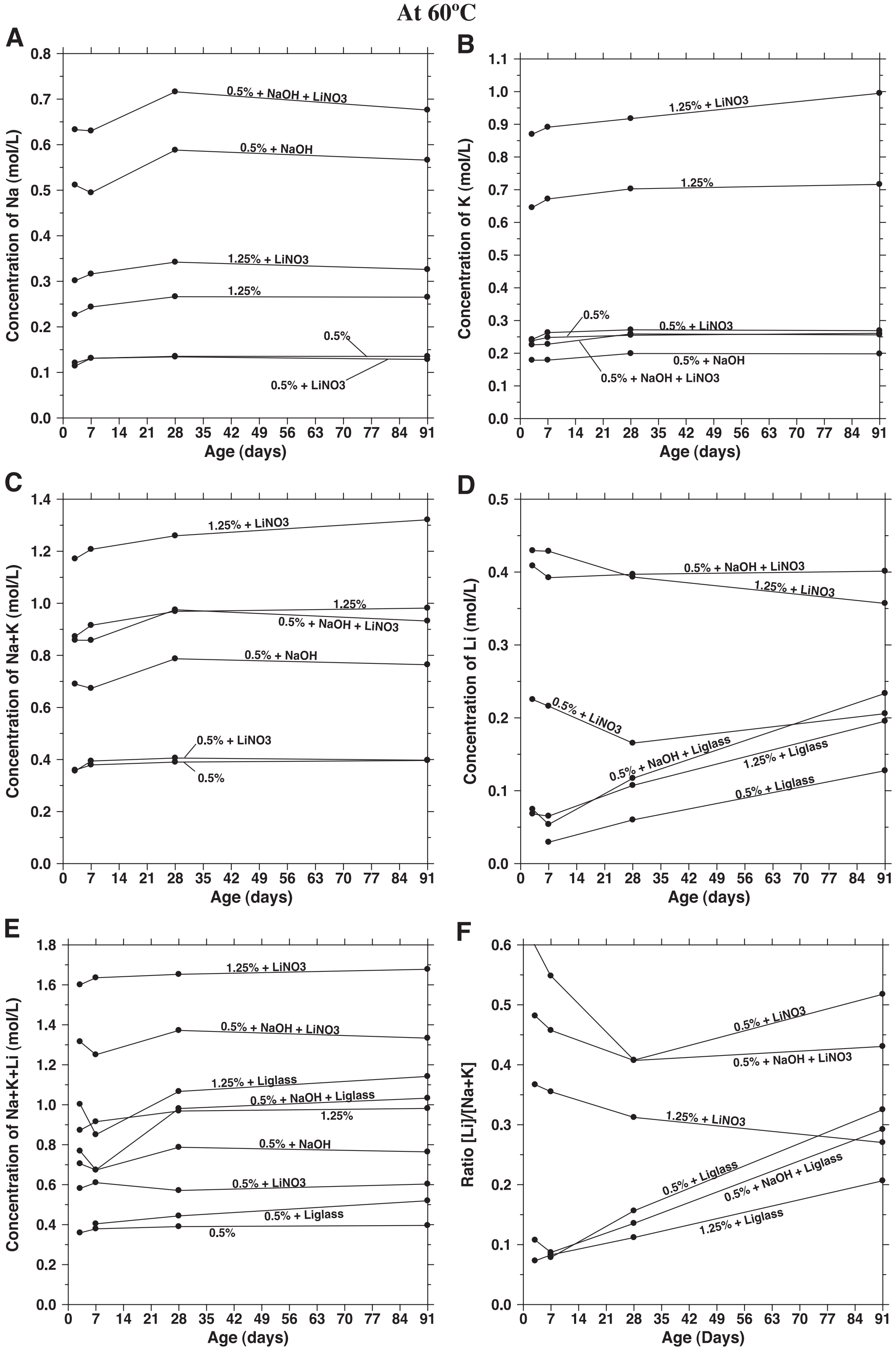

Fig. 3. Pore solution chemistry of cement pastes stored at 60 °C. (A) [Na^+]; (B) [K^+]; (C) [Na^++K^+]; (D) [Li^+]; (E) [Na^++K^++Li^+]; (F) [Li^+]−[Na^++K^+].

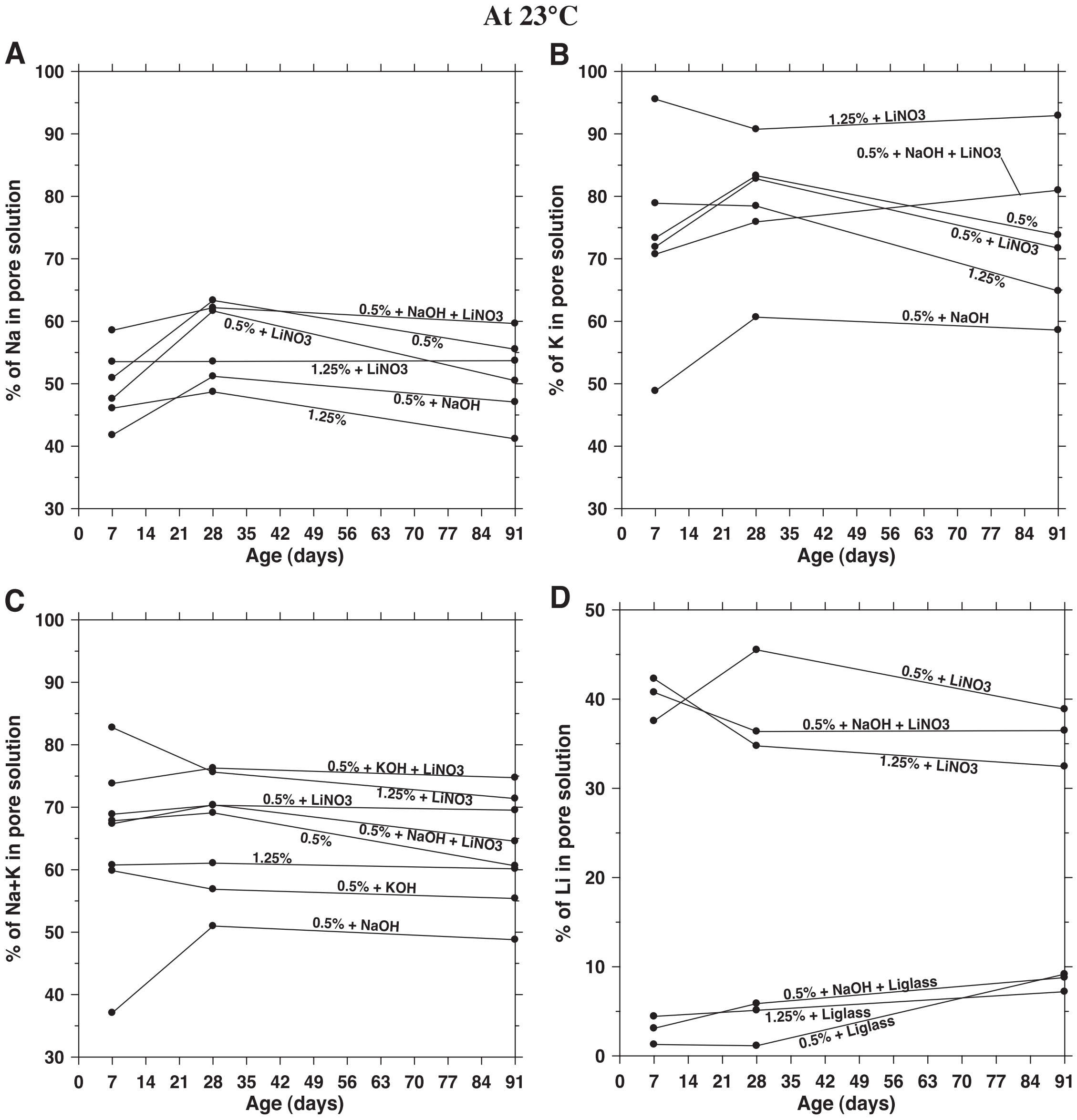

Fig. 4. Proportion of alkalis in the pore solution of cement pastes stored at 23 °C. (A) [Na^+]; (B) [K^+]; (C) [$Na^+ + K^+$]; (D) [Li^+].

mixtures (0.5%, 0.5%+NaOH, 0.5%+KOH, and 1.25%) and the mixtures containing $LiNO_3$.

- Independent of temperature, the proportions of Na, K, and Na+K in the pore solution of such mixtures tend to slightly increase up to 28 days, then to decrease slightly. However, it must be noted that for each mixture, only one measurement was made after 28 days.
- Also independent of temperature, the proportion of Li in the pore solution of the $LiNO_3$ mixtures generally tends to decrease more rapidly at early age, more likely because Li is readily available and incorporated in cement hydrates during this more active phase of hydration. This result agrees with Diamond [15] who reported that as much as half of the added lithium as $LiNO_3$ is incorporated in the cement hydrates during the period of active hydration. The lithium so removed from the pore solution is presumably not available for subsequent incorporation into ASR gel [15] or to prevent ASR.
- On average, for the $LiNO_3$ mixtures, the proportions of Na, K, and Li in the pore solution after 91 days are about 55%, 80%, and 35%, respectively (Figs. 4–6), and the effect of temperature is not very significant. It is clear that Li is incorporated in greater proportions than Na in the cement hydrates, which in turn is incorporated in greater proportions than K.
- The effect of $LiNO_3$ on the other alkali ions in the pore solution is also clear in the case of the high-alkali control and $LiNO_3$ mixtures; in the presence of $LiNO_3$, the proportions of Na and K in the pore solution significantly

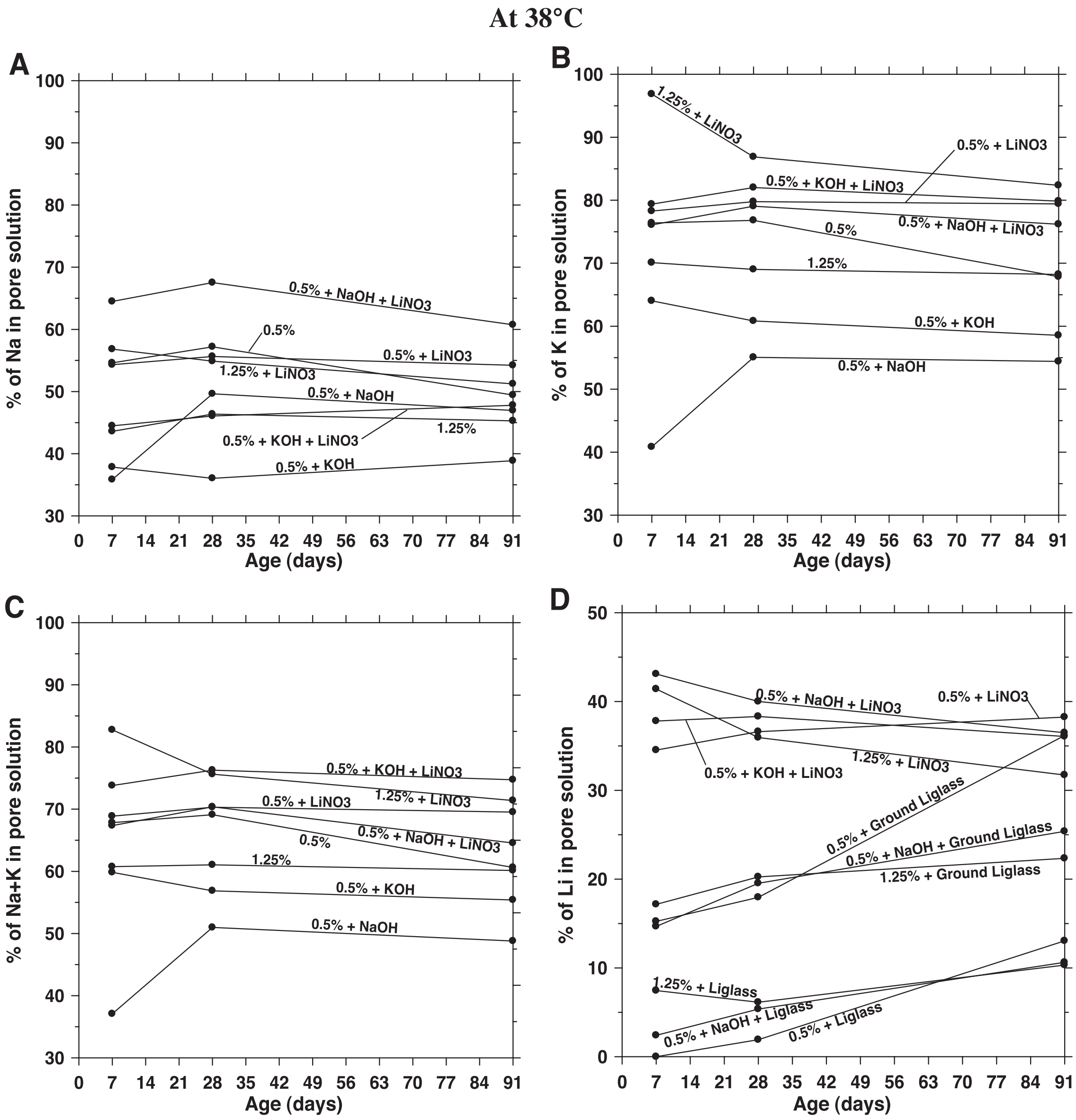

Fig. 5. Proportion of alkalis in the pore solution of cement pastes stored at 38 °C. (A) [Na^+]; (B) [K^+]; (C) [$Na^+ + K^+$]; (D) [Li^+].

increase (Figs. 4C, 5C, 6C for Na+K), which again supports the fact that Li is more preferentially incorporated in hydrates than Na and K.

- For the control and $LiNO_3$ mixtures made with the same total alkali content (i.e., 1.25% Na_2O_e, excluding Li), the proportions of Na, K, and Na+K in the pore solution tend to be highest when using the high-alkali cement and lowest when using the low-alkali cement plus NaOH, while the mixtures made with the same cement plus KOH fall between or approach the high-alkali cement mixtures (1.25%>0.5%+KOH>0.5%+NaOH; 1.25%+LiN=0.5%+KOH+LiN>0.5%+NaOH+LiN; Figs. 4C–6C). As mentioned before, based on the alkali concentrations, this suggests again that alkalis added as NaOH or KOH are slightly more completely incorporated in the cement hydrates than alkalis initially included in the anhydrous cement particles and that Na is more incorporated than K.

For the mixtures containing Li glass, the proportions of Li in the pore solution tend to progressively increase with time (Figs. 4D, 5D, and 6D); moreover, the higher the temperature (cf. Figs. 4D, 5D, and 6D) and the finer the glass (Fig. 5D), the greater the rate of release of Li and the greater the ultimate proportion of Li in the pore solution (i.e., after 91 days). These ultimate proportions for the as-received glass are around 9% at 23 °C, 12% at 38 °C °C, and 23% at 60 °C. In the mixtures incorporating the ground glass, tested only at 38 °C, the proportions at 91 days range from 20% to 35%. These results clearly demonstrate that the lithium as-received glass progressively dissolves at a relatively low rate in

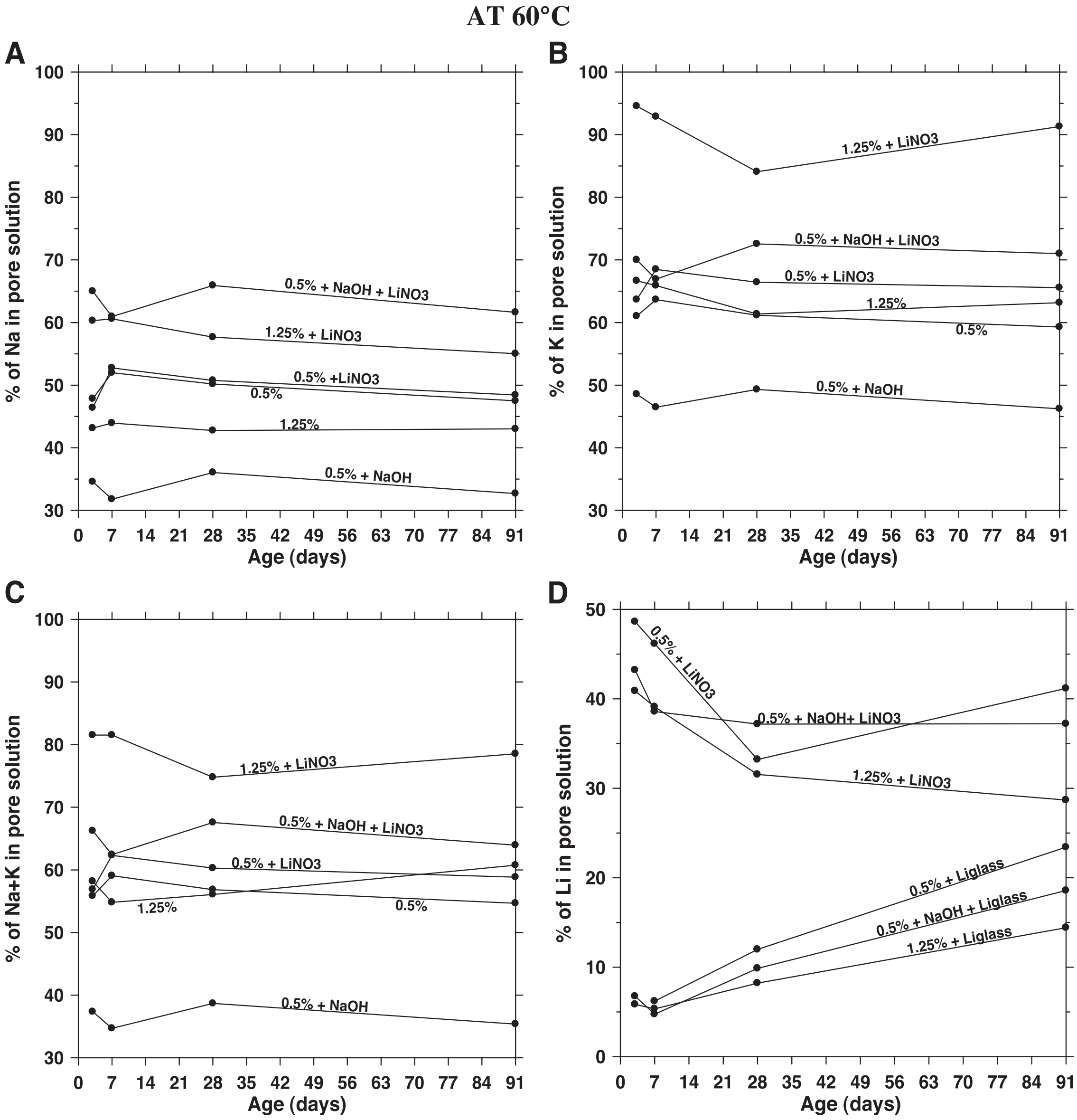

Fig. 6. Proportion of alkalis in the pore solution of cement pastes stored at 60 °C. (A) [Na^+]; (B) [K^+]; (C) [$Na^+ + K^+$]; (D) [Li^+].

the pore solution but that a fine grinding significantly improves its reactivity.

4.6. [Li]–[Na+K] molar ratio and total alkali contents of cement hydrates

Starting with an overall [Li]–[Na+K] ratio of 0.74 (Table 2) and considering that this ratio is usually less than 0.50 in the pore solutions (Table 3 and Figs. 1F, 2F, and 3F), this ratio is necessarily more than 0.74 in the solids. The high ratios observed for the Li glass mixtures are because there is still a large proportion of unreacted solid Li glass particles even after 91 days. However, for the $LiNO_3$ mixtures, the above ratio corresponds to the Li incorporated in the cement hydrates only. It varies between 1.1 and 1.6 for the 0.5%+LiN mixtures, 1.1 and 1.5 for the 0.5%+NaOH+LiN mixtures, 1.8 and 1.9 for the 0.5%+KOH+LiN mixtures, and 1.7 and 2.5 for the 1.25%+LiN mixtures. For the three series of high-alkali mixtures, the ratio is thus highest with the high-alkali cement, intermediate with the low-alkali cement plus KOH, and lowest with the same cement plus NaOH. These results agree with the highest, intermediate, and lowest proportions of Na and K in the corresponding pore solution, respectively. There is no clear variation of the [Li]–[Na+K] ratio in hydrates with time or temperature.

The total $\%Na_2O_e$ contents (including Li) in the cement hydrates of the control and $LiNO_3$ mixtures are illustrated in Fig. 7. These contents are equal to the sum of the three individual Na, K, and Li contents, expressed in moles of Na+K+Li per kilogram of solids (hydrates), multiplied by 0.031. One can note that the $\%Na_2O_e$ in

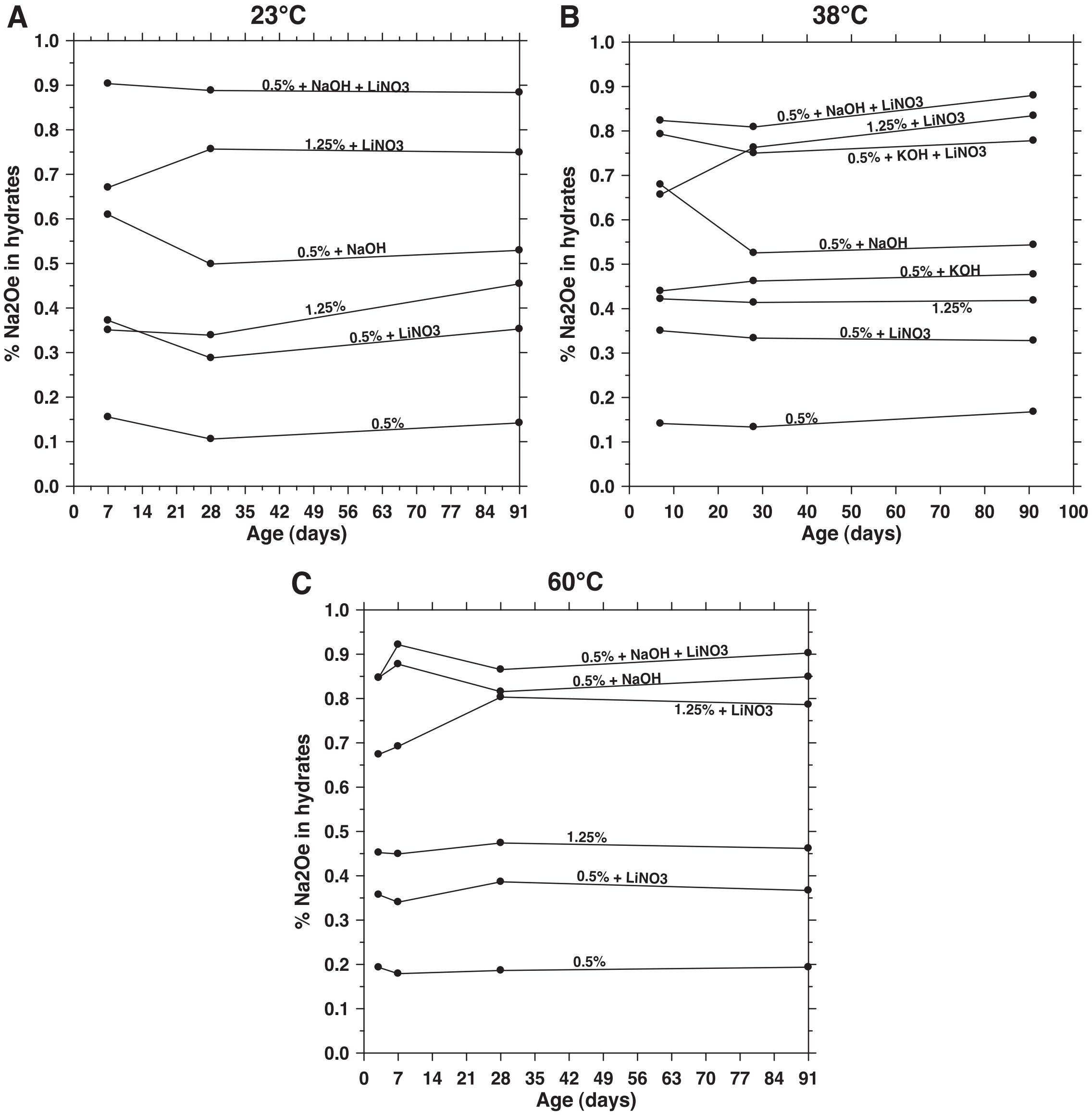

Fig. 7. %Na_2O_e (including Li) in the cement hydrates present in the control and $LiNO_3$ cement pastes. (A) 23 °C; (B) 38 °C; (C) 60 °C.

hydrates is relatively constant with time for each mixture and not significantly affected by temperature. The most important parameter is the total Na_2O_e in the original mixture: the higher this content, the higher the alkali content in the cement hydrates. A similar observation was made by Duchesne and Bérubé [23] in a study involving a variety of SCMs (two silica fumes, three fly ashes, and one blast-furnace slag). Evidently, in the present study, the total Na_2O_e content (including Li) in the original mixtures is higher when $LiNO_3$ is added to the mixture. For mixtures with same total alkali contents without lithium addition (e.g., 1.25% using the high-alkali cement, the low-alkali cement+NaOH, or the low-alkali cement+KOH), the alkali content of the cement hydrates is least with the high-alkali cement, intermediate with the low-alkali cement plus KOH, and highest with the same cement plus NaOH. Once again, this confirms that cement alkalis are less completely incorporated into the cement hydrates than alkalis already available in the pore solution at the time of mixing (i.e., as NaOH or KOH addition) and that Na is more incorporated than K (NaOH vs. KOH addition). However, the total alkali content in the hydrates of $LiNO_3$ mixtures is more constant, more likely because Li takes the place available in the hydrates when the other alkalis are less available.

5. Conclusion

This study on cement pastes was undertaken to better assess the effect of lithium on the chemistry of the pore solution and cement hydrates of hydraulic systems, and the effect of temperature. The following conclusions can be drawn:

- The pH of the pore solution generally decreased by about 0.1 when adding $LiNO_3$, while it increased by about 0.1 in the presence of a Li-bearing glass and by about 0.2 when this glass was finely ground.
- For the mixtures made with the Li glass, the $[Li^+]$ concentration increased with time, temperature, glass fineness (as-received glass vs. ground glass), and the $[Na^+ + K^+]$ concentration in the pore solution. The results obtained clearly demonstrate that the Li glass does not rapidly release lithium, at least under normal conditions of temperature and pH.
- On average, for the mixtures incorporating $LiNO_3$, the proportions of Na, K, and Li in the pore solution after 91 days (the oldest specimens tested) were about 55%, 80%, and 35% of the original load, respectively, and the effect of temperature was not very significant. It is clear that Li was incorporated into the cement hydrates in greater proportions than Na and K, with Na being always incorporated in greater proportions than K, even in the absence of Li.
- For all mixtures incorporating $LiNO_3$, the $[Li^+]$–$[Na^+ + K^+]$ molar ratio in the pore solution was usually between 0.30 and 0.45 (i.e., about half of the original value of 0.74). On the other hand, this ratio was always >1.1 in the cement hydrates. Both ratios were not significantly influenced by temperature and time.
- The total $\%Na_2O_e$ content (including Li) of the cement hydrates in the control and $LiNO_3$ mixtures was relatively constant with time for each mixture and was not significantly affected by temperature. However, the higher the total Na_2O_e content in the original mixtures, the higher the amount of alkalis incorporated into the cement hydrates.
- The overall chemistry of the pore solution and the cement hydrates appear not significantly influenced by temperature, at least between 23 and 60 °C. This supports the efforts currently done to develop accelerated test methods at relatively high temperatures for evaluating the effectiveness against ASR of Li-based products (e.g., a concrete prism test performed at 60 °C).
- The proportion of pore water expressed under 1000 MPa represented only between 5% and 26% of the total water content and was often less than 10% after 91 days. A somewhat greater percentage of the pore solution was generally expressed from the mixtures stored at 60 °C, especially after 91 days, possibly because of a more easily compressible microstructure.

Acknowledgements

This study was financially supported by Euclid Admixtures Canada and the National Science and Engineering Research Council of Canada (NSERC).

References

[1] CSA A23.1-00, Concrete Materials and Methods of Concrete Construction, Appendix B – Alkali-aggregate reaction, Canadian Standards Association, Rexdale, Ontario, Canada, 2000.

[2] W.J. McCoy, A.G. Caldwell, New approach in inhibiting alkali–aggregate expansion, ACI Materials Journal 22 (9) (1951) 693–706.

[3] M. Lawrence, H.F. Vivian, The reactions of various alkalies with silica, Australian Journal of Applied Science 12 (1961) 96–103.

[4] Y. Sakaguchi, M. Takakura, A. Kitagawa, T. Hori, F. Tomosawa, M. Abe, The inhibiting effect of lithium compounds on ASR, 8th International Conference on AAR in Concrete, Society of Materials Sciences of Japan, Kyoto, Japan, 1989, pp. 229–234.

[5] Y. Ohama, K. Demura, M. Kakegawa, Inhibiting alkali–aggregate reaction with chemical admixtures, 8th International Conference on AAR in Concrete, Society of Materials Sciences of Japan, Kyoto, Japan, 1989, pp. 253–258.

[6] D. Stark, Lithium salt admixtures—An alternative method to prevent expansive alkali–silica reactivity, 9th International Conference on AAR in Concrete, The Concrete Society, Wexham, UK 1992, pp. 1017–1025.

[7] D. Stark, B. Morgan, P. Okamoto, S. Diamond, Eliminating or minimizing the risk of alkali–silica reactivity, National Research Council, Strategic Highway Research Program (SHRP), SHRP-C 343, 1993, 266 pp.

[8] M.D.A. Thomas, D.B. Stokes, Use of a lithium-bearing admixture to suppress expansion in concrete due to alkali–silica reaction, Transportation Research Record 1668 (1999) 54–59.

[9] M.D.A. Thomas, R. Hooper, D.B. Stokes, Use of lithium-containing compounds to control expansion in concrete due to ASR, 11th International Conference on AAR in Concrete, Centre de recherche sur les infrastructures de béton (CRIB), Laval University, Québec City, Canada, 2000, pp. 783–792.

[10] D.B. Stokes, C.E. Manissero, Use of lithium-based admixture to control ASR expansion, 14th Reunion Tecnica Asociacion Argentina de Tecnologia del Hormigon, Universidad Nacional del Centro de la Provincia de Buenos Aires, Argentina, 2001, 10 pp.

[11] B. Fournier, D.B. Stokes, A. Ferro, Comparative field and laboratory investigations on the use of supplementary cementing materials and lithium-based admixtures to control expansion due to alkali–silica reaction in concrete, 6th International CANMET/ACI Conference on Durability of Concrete, Thessaloniki, Greece, Supplementary Papers 2003, pp. 823–851. ICON-CANMET, Ottawa, Canada.

[12] J.S. Lumley, ASR suppression by lithium compounds, Cement and Concrete Research 27 (2) (1997) 235–244.

[13] B. Durand, More results about the use of lithium salts and mineral admixtures to inhibit ASR in concrete, 11th International Conference on AAR in Concrete, Centre de recherche sur les infrastructures de béton (CRIB), Laval University, Québec City, Canada, 2000, pp. 623–632.

[14] S. Diamond, S. Ong, The mechanisms of lithium effects on ASR, 9th International Conference on AAR in Concrete, The Concrete Society, Wexham, UK, 1992, pp. 269–278.

[15] S. Diamond, Unique response of $LiNO_3$ as an alkali silica reaction-preventive admixture, Cement and Concrete Research 29 (8) (1999) 1271–1275.

[16] D.B. Stokes, H.H. Wang, S. Diamond, A lithium-based admixture for ASR control that does not increase the pore solution pH, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Roma, Italy, ACI SP, vol. 173, 1977, pp. 855 1271–868. American Concrete Institute, Farmington Hills, USA.

[17] X. Mo, C. Yu, Z. Xu, Long-term effectiveness and mechanism of LiOH in inhibiting alkali–silica reaction, Cement and Concrete Research 33 (1) (2003) 115–119.

[18] L.D. Mitchell, J.J. Beaudoin, P. Grattan-Bellew, The effects of lithium hydroxide solution on alkali silica reaction gels created with opal, Cement and Concrete Research 34 (4) (2004) 641–649.

[19] B.Q. Blackwell, M.D.A. Thomas, A. Sutherland, Use of lithium to control expansion due to alkali – silica reaction in concrete containing U.K. aggregates, 4th CANMET/ACI International Conference on Concrete Durability, Sydney, Australia, ACI SP, vol. 170, 1997, pp. 649 – 663. American Concrete Institute, Farmington Hills, USA.

[20] K.J. Folliard, M.D.A. Thomas, K.E. Kurtis, Guidelines for Use of Lithium to Mitigate or Prevent ASR, Publication No. FHWA-RD03-047 2003. 61 pp.

[21] M.A. Bérubé, J. Duchesne, Evaluation of testing methods for assessing the effectiveness of mineral admixtures in suppressing expansion due to alkali – aggregate reaction, 4th CANMET-ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, Turkey, ACI SP, vol. 132, 1992, pp. 549 – 575. American Concrete Institute, Farmington Hills, USA .

[22] M. De Grosbois, É. Fontaine, Performance of the 60 °C-accelerated concrete prism test for the evaluation of potential alkali-reactivity of concrete aggregates, 11th International Conference on AAR in Concrete, Centre de recherde sur les infrastructures de béton (CRIB), Laval University, Québec City, Canada, 2000, pp. 277 – 286.

[23] J. Duchesne, M.A. Bérubé, Effect of supplementary cementing materials on the composition of cement hydration products, Advanced Cement Based Materials 2 (2) (1994) 43 – 52.