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Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity

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Abstract

In Phase I, particles from 17 different aggregates, 1.25–5 mm in size, were immersed in continuously agitated solutions at 38 °C: distilled water, $Ca(OH)_2$-saturated solution, 0.7 M NaOH (measurement of K supply), and 0.7 M KOH (measurement of Na supply). These solutions were periodically analysed for K and/or Na up to 578 days. More alkalies were released in alkaline solutions than in lime-saturated solution, with lower values in water. After 578 days, the aggregates released between $<0.01\%$ and 0.19% Na_2O_e, excluding the nepheline-rich aggregate tested (0.68%). This would correspond to a contribution to concrete from <0.1 to 3.4 kg/m^3 Na_2O_e (12.7 for the phonolite), based on an aggregate content of 1850 kg/m^3. In general, the feldspar-rich aggregates released significantly more alkalies. In Phase II, the water-soluble alkali content of mass concrete elements from many dams was measured using a hot water extraction method. The values obtained often largely exceed the soluble alkali content expected to be released by the cement used. These results thus also suggest that large amounts of alkalies were supplied with time by the aggregates, particularly by feldspar-rich ones.

Keywords: Aggregates; Alkalies; Alkali–aggregate reaction; Concrete structures; Leaching tests

1. Introduction

1.1. Conditions for ASR

Three essential conditions must be satisfied to initiate and sustain alkali–aggregate reactions in concrete: (1) the aggregates are potentially reactive; (2) the alkali concentration is high in the concrete pore solution; and (3) the concrete is exposed to high humidity conditions. The alkali concentration must be sufficiently high in the concrete pore fluid for sufficient hydroxide ions to be present to initiate and maintain alkali–silica reaction (ASR) in a concrete element. Normally, the higher the alkali concentration, the greater the expansion due to ASR. In fact, OH^- anions are liberated from the portlandite $Ca(OH)_2$ in order to approach equilibrium with the alkali cations. So the higher the amount of alkali ions in the pore solution, the higher the pH, and the higher the risk for ASR. In general, the soluble alkalies are mostly supplied by the cement, but some may also be provided by chemical admixtures or mineral additions, by the mixture water (salt), by the aggregates, or by secondary sources such as seawater, deicing salts, and industrial brines.

1.2. Preventive measures

Using a low-alkali cement with less than 0.6% Na_2O_e or limiting the concrete alkali content constitutes the most popular way to ensure that the alkali concentration is low enough in the concrete pore fluid to minimize ASR in the presence of potentially reactive aggregates. The most recent version of the Canadian standard CSA A23.1 set the above limit between 1.7 and 3 kg/m^3 Na_2O_e according to the type of concrete structure to built and to the exposure conditions, which takes account for the contributions by cement, mineral additions, chemical additives, and mixture water

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[1,2]. Because of limited information in these respects, this standard does not take account for aggregates and external sources of alkalies. However, it is the opinion of the authors that exposure to seawater or deicing salt should not initiate ASR problems in low-alkali concrete elements incorporating reactive aggregates [3].

1.3. Alkali contribution by aggregates

According to many authors, some aggregates or mineral phases present within the aggregate particles may also, with time, supply significant amounts of alkalies to the concrete pore solution, such as volcanic glasses, unwashed marine sands, alterated feldspars, micas, clay minerals and zeolites [4–13]. This could explain why many concrete structures are affected by ASR, although built with low-alkali cements ($< 0.6\%$ Na_2O_e) and/or with cements supplying less than 3 kg/m^3 Na_2O_e, and even less than 2 kg/m^3, as in the case of many dams reported by Bérubé et al. [14].

1.4. Test procedure for evaluating the alkali contribution by aggregates

A number of experimental procedures have been used in the past to estimate the alkali contribution by aggregates to the concrete pore solution [4,7,11,15] (Table 1). However, the number and types of aggregates tested were limited, and the test conditions such as the aggregate fineness, the solution used for extraction, the aggregate/solution ratio, the temperature, and the test duration greatly varied from one study to another. All these conditions influence the rates of alkali leaching as well as the absolute amounts of alkalies released. Moreover, the most aggressive solution used for extraction was a saturated lime solution, for instance in the procedure proposed in France by LCPC [15], often with no solid lime in excess (see Table 1), which is much less aggressive than in normal concrete. Indeed, according to Diamond [16], the OH^- concentration in the pore solution of a concrete made with a water/cement ratio of 0.5 and a cement containing 1% Na_2O_e, for instance, is around 0.74 M (pH $\approx$ 13.85) after 28 days, which is 34 times more than in a saturated lime solution ($[OH^-] \approx 0.021$ M and pH $\approx$ 12.32 *at 38 °C*), and even more in the long term as a result of a more complete hydration, which decreases the amount of pore water. Also, the lower the water/cement ratio, the higher the alkali concentration in the pore water. Moreover, when a saturated lime solution is used for extraction of alkalies with no solid lime in excess, the OH^- concentration progressively decreases as a result of chemical reactions with aggregate particles. In a real concrete, there is a lot of solid portlandite to supply OH^- ions to the pore solution.

Table 1
Procedures used to evaluate the alkali contribution by aggregates

Test conditions	Van Aardt and Visser [4]	Stark and Bhatty [7]	Kawamura et al. [11]	LCPC [15]	This study
Aggregates or minerals	6 feldspars, 2 clay minerals	3 feldspars, 3 sands, 3 gravels, 1 andesite	2 andesites	standard procedure	17 different types
Aggregate fineness	0.5 g, powdered	(1a,1b,1c) 5 g, < 80 μm (2) 675 g, 0.15–5 mm (C 227 grading)	100 g, 0.15–5 mm (C 227 grading)	500 g, as used in concrete (but < 20 mm)	40 g, 1–5 mm (some tests: 0.63–1 mm)
Extraction solution	0.5 g of lime in 25 ml of water (lime saturated + excess lime)	(1a,1b) 25 ml of lime saturated (1c) 25 ml of distilled water (2) 500 ml of lime saturated	200 ml of lime saturated	20 g of lime in 300 ml of distilled water (lime saturated + excess lime)	40 ml of: • distilled water • lime saturated + excess lime • 0.7 N NaOH • 0.7 N KOH
Aggregate solution	1:50	(1a,1b,1c) 1:5 (2) 1:0.74	1:2	1:0.6	1:1
Temperature	39 °C	(1a,2) 38 °C (1b,1c) 80 °C	40 °C	100 °C (boiling)	38 °C
Agitation	–	Conditions (1a) and (2)	–	–	Yes
Test period	250 days	(1a) 7–90 days (1b,1c) 28 days (2) 7–180 days	1–180 days	7 days	7–578 days
Percent soluble Na_2O_e[a]	0.01–2.32	(1a) 0.31–1.99 (10)[b,c] (1b) 0.83–5.03 (4)[b] (1c) 0.03–0.13 (4)[b] (2) 0.07 (1)[b,d]	0.02 and 0.07	–	0.003–0.68

[a] Maximum values obtained during the test period (usually at the end), by mass of aggregate.

[b] Number between parentheses corresponds to the number of aggregates tested.

[c] 0.45–1.99 for the four aggregates tested under Conditions (1b) and (1c).

[d] The aggregate tested gave 0.45 under Condition (1a).

1.5. Alkali migration inside concrete elements

A number of studies suggested that alkalies can migrate and locally concentrate in a concrete element, which can then locally initiate or accelerate ASR. Nixon et al. [17], Nixon and Gillson [18], and Stark [19] observed a significant increase in the concentration of alkali ions close to the surface of concrete members from which moisture is evaporating, with local very high concentrations that have been shown by Nixon et al. [17] to be due to the crystallisation of alkali sulfates. Stark and Bhatty [7] report that volcanic aggregates caused AAR problems with very low alkali cements (0.35% Na_2O_e) as a result of local concentration of alkali due to wetting and drying and/or to alkali releases from the aggregates. Alkali ion migration in concrete should be promoted by a higher water/cement ratio (higher permeability), and could explain why low alkali concrete may locally develop ASR.

1.6. Test procedure for evaluating the soluble alkali content of concrete

A hot water extraction method is currently used in Canada to determine the water-soluble or active alkali content of field concretes, expressed in kilograms per cubic meter Na_2O_e [20,21]. These measurements are performed for diagnosis, i.e., for determining whether or not this content is sufficient for ASR to take place, as well as for prognosis. The method was investigated in detail by Bérubé et al. [21]. However, a clear distinction must be made between total alkalies (usually restricted to the total amount of alkalies supplied by the cement) and soluble alkalies (those measured in the hot water extraction method). In fact, a significant amount of alkalies remains incorporated in cement hydrates and, in the presence of ASR, in the products from this reaction [21]. Previous studies [22,23] indicated that OPC hydrates contain about 0.4–0.5% Na_2O_e, which is close to the value of 0.37% obtained in a more recent study [21], while much higher contents can be obtained in the presence of supplementary cementing materials (SCMs), and particularly with high-alkali fly ash [23]. The results by Diamond [16] and Duchesne and Bérubé [23] also suggest that the amount of alkalies incorporated in the cement hydrates is about proportional to the total amount of alkalies contained in the cement. Based on this assumption, one may consider that about 40% of the total alkalies from the cement is incorporated in cement hydrates. In such a situation, the above safe limit of 3 kg/m^3 in terms of total Na_2O_e should correspond to about 1.8 kg/m^3 in terms of soluble Na_2O_e. Based on the results obtained by Bérubé et al. [21], the hot water extraction method is considered able to extract most alkalies originally dissolved in the concrete pore solution before the concrete was dried, while not extracting the alkalies incorporated in the cement hydrates and most of those incorporated progressively in the products from ASR. However, the results obtained in the method must be corrected for the alkali contribution by the aggregates in the test method [21].

1.7. Objectives of this study

This study was undertaken: (1) to propose a test method to better estimate the amounts of alkalies that can be supplied to the concrete pore solution by the aggregates in the long term, using experimental conditions that better simulate the chemistry of the pore solution in normal concretes, and (2) to evaluate these amounts for a wide variety of Canadian aggregates from Québec and Ontario. In the meantime, measurements of the water-soluble alkali content of the concrete from a large number of hydraulic structures, at different depths in some case, were performed in order: (3) to validate or disprove the results obtained above about the potential alkali contributions by aggregates, and (4) to investigate the actual potential for alkali migration and local concentration within the whole mass of concrete elements. The most important objective is to propose modifications to the current standards in order to reasonably account for the potential alkali contribution by aggregates in the case of new concrete structures to be built with reactive or potentially reactive aggregates.

2. Materials and methods

2.1. Tests on aggregate particles

Seventeen aggregates representative of the various types of concrete aggregates exploited in Québec and Ontario, Canada, were selected and chemically analysed. They present different alkali contents and various degrees of alkali reactivity (see Table 2). They were crushed and screened to optimize the amount of material of 1.25–5 mm in size.

For each aggregate, 40-g subsamples of particles of the above size were placed in 60-ml-capacity Nalgene bottles with 40 ml of various solutions: (1) distilled water (for measurement of K and Na supplies), (2) lime-saturated solution with an excess of 1 g of solid lime (measurements of K and Na supplies), (3) 0.7 N NaOH (measurement of K supply), and (4) 0.7 N KOH (measurement of Na supply). The solutions were maintained at 38 °C with the samples continuously rolling for 578 days.

After 7, 28, 112, 335, and 578 days, the bottles were allowed to rest for 24 h at room temperature, for particle settling, then 10-ml samples of solution were taken out by pipetting, and replaced by the same amount of the corresponding original solution. The samples were then returned to 38 °C until the next measurement. All solution samples were analysed by atomic absorption for K and/or Na, after being acidified. In each series of analyses, the

Table 2
Cumulative amounts of alkalies released by the aggregates after 578 days

				Soluble alkalies										
	Total alkalies			Pure water			Lime solution			Alkaline solutions			Maximum Na_2O_e[a]	
Aggregate	Na_2O (%)	K_2O (%)	Na_2O_e (%)	Na_2O (%)	K_2O (%)	Na_2O_e (%)	Na_2O (%)	K_2O (%)	Na_2O_e (%)	Na_2O[b] (%)	K_2O[b] (%)	Na_2O_e (%)	(%/total)[c]	(kg/m^3)[d]
Phonolite	9.09	4.88	12.30	0.130	0.031	0.151	0.100	0.015	0.110	0.560	0.189	0.684	5.56	12.65
Granite	3.50	4.83	6.68	0.024	0.045	0.053	0.026	0.084	0.081	0.059	0.192	0.185	2.77	3.43
Rhyolitic tuff[e]	5.25	1.70	6.37	0.053	0.010	0.059	0.065	0.018	0.077	>0.053	>0.022	>0.067	>1.24	>1.47
Granitic sand	2.85	3.65	5.25	0.013	0.022	0.028	0.019	0.016	0.030	0.010	0.031	0.030	0.75	0.73
Diorite	4.49	1.13	5.23	0.028	0.006	0.032	0.038	0.023	0.053	0.136	0.065	0.179	3.42	3.31
Granitic gneiss	3.57	2.01	4.89	0.021	0.022	0.036	0.027	0.038	0.052	0.076	0.095	0.139	2.84	2.57
Andesite	4.47	0.12	4.55	0.047	0.001	0.048	0.056	0.001	0.057	0.101	0.002	0.102	2.25	1.89
Lithic gravel (Sudbury)[f]	3.01	2.03	4.35	0.033	0.006	0.036	0.042	0.014	0.052	0.146	>0.032	>0.166	>3.83	>3.08
Greywacke	2.33	2.60	4.04	>0.026	0.015	>0.036	0.025	0.012	0.033	0.108	>0.055	>0.145	>3.58	>2.68
Shale[e]	0.98	3.41	3.22	0.044	0.026	0.061	0.036	0.022	0.050	0.034	0.020	0.047	1.88	1.12
Dolostone (Beekmantown)[f]	0.04	2.62	1.76	0.004	0.056	0.041	0.004	0.085	0.060	0.008	0.184	0.129	7.33	2.39
Dolostone limestone (Kingston)[e]	0.06	0.30	0.26	0.004	0.010	0.011	0.007	0.016	0.017	0.018	0.059	0.057	21.98	1.05
Siliceous limestone (Trenton)[g]	0.11	0.24	0.27	0.009	0.003	0.010	0.012	0.002	0.013	0.011	0.003	0.013	5.00	0.25
Pure limestone (Trenton)	< 0.10	0.09	< 0.16	0.003	0.003	0.005	0.013	0.010	0.019	0.007	0.015	0.017	14.41	0.42
Siliceous limestone (Spratt)[e]	0.04	0.08	0.09	0.003	0.003	0.005	0.003	0.003	0.004	0.006	0.005	0.009	9.24	0.16
Siliceous sandstone (Potsdam)[g]	0.01	< 0.05	< 0.04	0.001	0.008	0.007	0.001	0.006	0.005	>0.002	>0.014	>0.011	>25.60	>0.20
Quartzite	< 0.01	< 0.05	< 0.04	0.000	0.001	0.001	0.001	0.001	0.002	>0.002	>0.002	>0.004	>8.05	>0.06
Average	2.35	1.75	3.50	0.026	0.016	0.036	0.028	0.022	0.042	0.079	0.058	0.117	>7.04	>2.20

[a] Maximum Na_2O contribution + maximum K_2O contribution in water, lime solution, or alkaline solutions, most of time corresponding to alkaline solutions.

[b] Na_2O contribution measured in 0.7 N KOH and K_2O contribution measured in 0.7 N NaOH. The sign > signifies that the analysis was not performed after 11 months (greywacke and quartzite) and sometimes even after 4 months (Potsdam, tuff and Sudbury), due to precipitation of silica gel when the solution samples were acidified.

[c] Percentage of total alkalies (Na_2O_e) in the aggregate.

[d] Based on a total concrete aggregate content of 1850 kg/m^3.

[e] Highly reactive aggregate; alkali–silica reactivity except for the dolomitic limestone (alkali–carbonate reactivity).

[f] Slowly/marginally reactive aggregate; alkali–silica reactivity.

[g] Moderately reactive aggregate; alkali–silica reactivity.

Table 3
Dams investigated, soluble alkali content, and estimated contributions by aggregates

Hydraulic dams	Sampled elements	Core number (number of samples analyzed)	Nature of aggregates		Measured soluble Na_2O_e (kg/m^3)[a]	Cement content (kg/m^3)[b]	Percent Na_2O_e in the cement[b]	Expected soluble Na_2O_e (kg/m^3)[c]	Aggregate contribution (kg/m^3)[d]
			Coarse	Fine					
Castor	?	1,2,3 (1)	gran. gn.	gran. sand	2.36	(275)	(1.0)	1.65	0.71
Melville	Pillar 7	11 (4)	gran. gn.	gran. sand	3.50	(275)	(1.0)	1.65	1.85
Melville	Pillar 9	15 (4)	gran. gn.	gran. sand	4.34	(275)	(1.0)	1.65	2.70
Melville	Pillar 12	19 (3)	gran. gn.	gran. sand	3.04	(275)	(1.0)	1.65	1.39
La Gabelle	left dam	27 (1)	gran. gn.	gran. sand	0.20	(275)	(1.0)	1.65	0
Rapides 7	Pillar 13	7,8 (1)	gran. gn.	gran. sand	4.30	(275)	(1.0)	1.65	2.65
St-Narcisse	Pillar	5 cores (1)	gran. gn.	gran. sand	1.40	(275)	(1.0)	1.65	0
Farmers	Cursor 27	22 (1)	gran. grav.	gran. sand	2.48	(275)	(1.0)	1.65	0.83
	Cursor 7	28 (1)	gran. grav.	gran. sand	4.01	(275)	(1.0)	1.65	2.36
	Cursor 1	34 (1)	gran. grav.	gran. sand	3.54	(275)	(1.0)	1.65	1.89
	Pillar 5	31 (5)	gran. grav.	gran. sand	2.46	(275)	(1.0)	1.65	0.81
	Pillar 14	24 (5)	gran. grav.	gran. sand	3.03	(275)	(1.0)	1.65	1.38
Hemmings	?	2 (1)	lith. grav.	lith. sand	2.59	(275)	(1.0)	1.65	0.94
	?	3 (1)	lith. grav.	lith. sand	1.39	(275)	(1.0)	1.65	0
Mitis 2	?	B (1)	lith. grav.	lith. sand	1.70	(275)	(1.0)	1.65	0.05
Lac Mitis	?	1 (2)	lith. grav.	lith. sand	1.62	(275)	(1.0)	1.65	0
Mistigoug.	?	1 (2)	lith. grav.	lith. sand	1.88	(275)	(1.0)	1.65	0.23
	?	B (1)	lith. grav.	lith. sand	1.70	(275)	(1.0)	1.65	0.05
Rapides 15	Pillar 5	5 (1)	lith. grav.	lith. sand	3.00	(275)	(1.0)	1.65	1.35
Up. Salmon	?	1 (1)	diorite	lith. sand	2.69	(275)	(1.0)	1.65	1.04
	?	2 (1)	diorite	lith. sand	3.21	(275)	(1.0)	1.65	1.56
	?	3 (1)	diorite	lith. sand	2.53	(275)	(1.0)	1.65	0.88
Sartigan	Pillar 19	1 (2)	rhyol. tuff	lith. sand	3.10	(275)	1.3	2.15	0.95
	upst. wall	3 (2)	rhyol. tuff	lith. sand	2.79	(275)	1.3	2.15	0.65
	Pillar 8	7 (1)	rhyol. tuff	lith. sand	2.75	(275)	1.3	2.15	0.60
	Pillar 6	9 (2)	rhyol. tuff	lith. sand	3.08	(275)	1.3	2.15	0.94
	Pillar 5	10 (1)	rhyol. tuff	lith. sand	2.98	(275)	1.3	2.15	0.84
Mercier	?	9,10 (1)	dol. + gr.gn.	gran. sand	1.69	(275)	(1.0)	1.65	0.04
Coteau 3	Pillar 15	34 (5)	dolostone	gran. sand	2.69	(275)	(1.0)	1.65	1.04
Coteau 2	Pillar 2	20 (4)	dolostone	lith. sand	2.60	(275)	(1.0)	1.65	0.95
Coteau 1	Pillar 17	4 (4)	dolostone	sil. sandst.	2.23	(275)	(1.0)	1.65	0.58
Les Cèdres	intake	1 (1)	dolostone	gran. sand	1.35	(275)	(1.0)	1.65	0
	evacuator	17 (1)	dolostone	gran. sand	2.70	(275)	(1.0)	1.65	1.05
	aspirator	3 (1)	sil. sandst.	gran. sand	2.43	(275)	(1.0)	1.65	0.78
Riv. Prairie	Pillar 8	11 (1)	sil. lim.	gran. sand	0.24	(275)	(1.0)	1.65	0
	gr. 7, spier	16 (1)	sil. lim.	gran. sand	1.32	(275)	(1.0)	1.65	0
	ev. pil. 2	19,19A (1)	sil. lim.	gran. sand	1.75	(275)	(1.0)	1.65	0.10
	left dam	18 (1)	sil. lim.	gran. sand	1.83	(275)	(1.0)	1.65	0.18
	overflow	8 (1)	sil. lim.	gran. sand	2.21	(275)	(1.0)	1.65	0.56
	Pillar 26	10 (1)	sil. lim.	gran. sand	2.63	(275)	(1.0)	1.65	0.98
	gr. 2, wall	2,2A (1)	sil. lim.	gran. sand	2.96	(275)	(1.0)	1.65	1.31
	ev. pil. 12	20,20A (1)	sil. lim.	gran. sand	3.60	(275)	(1.0)	1.65	1.95
	ev., border	21 (1)	sil. lim.	gran. sand	4.66	(275)	(1.0)	1.65	3.01
Pont-Rouge	?	1 (1)	sil. lim.	gran. sand	0.40	(275)	(1.0)	1.65	0
Juillet 1	Pillar 4	2 (5)	sil. sandst.	gran. sand	3.11	(275)	(1.0)	1.65	1.46
Juillet 2	Pillar 3	7 (7)	sil. sandst.	gran. sand	3.10	(275)	(1.0)	1.65	1.45
Beauharnois	Plot 2	C (6)	sil. sandst.	sil. sandst.	1.57	(275)	(1.0)	1.65	0
		D (7)	sil. sandst.	sil. sandst.	1.85	(275)	(1.0)	1.65	0.20
	Plot 4	A (7)	sil. sandst.	sil. sandst.	1.25	(275)	(1.0)	1.65	0
		B (7)	sil. sandst.	sil. sandst.	1.08	(275)	(1.0)	1.65	0

[a] Corrected for aggregate contribution in the test method.

[b] Estimated values between brackets.

[c] Assuming no aggregate contribution and 40% of cement alkalies in hydrates, which are not leached in the test.

[d] Measured soluble Na_2O_e content − expected soluble Na_2O_e from the cement.

four stock solutions were also analysed. The cumulative amounts of potassium and sodium released by the aggregates with time were corrected for the corresponding amounts in the stock solutions as well as for the amounts removed from the containers when sampling the solutions for the periodic measurements.

2.2. Tests on concrete cores

2.2.1. Concrete structures investigated

During the past 12 years, the water-soluble alkali content of core samples taken in many hydraulic structures, mostly Hydro Québec dams, either or not affected by ASR, has been measured using the hot water extraction method (Table 3). More recently, measurements were also performed on core samples taken at different depths along four vertical boreholes in two plots belonging to the Beauharnois dam, and along horizontal boreholes going through massive pillars belonging to other Hydro Québec dams: one pillar each for the Juillet I and II and Coteau I, II, and III dams, three pillars for the Melville dam (nos. 7, 9, and 12), and two pillars for the Farmers dam (nos. 5 and 14); alkali profiles were thus obtained in these concrete elements.

2.2.2. Sample preparation and chemical analyses

For the tests, all concrete samples were ground to pass the 160-μm sieve, as suggested by Bérubé et al. [21]. For better precision, all ground samples from the same structure were analysed at the same time (same series of measurements). More precisely, we proceeded as follows.

(1) Two 10-g subsamples of each ground concrete sample belonging to the same concrete element, and one subsample of a ground control concrete with a well-known soluble-alkali content, were immersed in 100 ml of boiling water for 10 min.

(2) The pulp was allowed to rest until the day after at room temperature.

(3) The pulp was then filtered with the solids retained and washed with distilled water, and the volume of solution was adjusted to 100 mm by adding distilled water.

(4) The Na and K concentrations of the solution were measured by atomic emission.

(5) The average results for the two subsamples of each concrete sample were expressed in the form of kilograms per cubic meter Na_2O_e, using an estimate of 2400 kg/m^3 for the concrete density.

(6) All results were corrected with respect to the value obtained for the control concrete (corrected value = measured value × known value for the control/measured value for the control).

(7) All results were also corrected for the estimated alkali contribution by the aggregates in the test method, using the values obtained by Bérubé et al. [21] for aggregates similar to those present in each concrete element tested, assuming aggregate contents of 1050 kg/m^3 for the coarse aggregate and 700 kg/m^3 for the fine aggregate.

2.2.3. Estimation of alkali contribution by aggregates

Based on known or estimated amount of total alkalies originally supplied by the cement to the concrete under test (= cement dosage in kg/m^3 × cement alkali content in %Na_2O_e), the amount of alkalies supplied by the aggregates since the construction of the corresponding concrete component was then estimated assuming that 40% of all alkalies from the cement was incorporated in the cement hydrates while not leached out in the test method, as suggested by Bérubé et al. [21]. In other words: alkali contribution by aggregates since the construction = [estimated or known amount of total alkalies from the cement × 60%] − water-soluble concrete alkali content (after correction with respect to the control concrete tested in parallel (Step 6 above) and for the alkali contribution by the aggregates in the test method (Step 7 above)). The value of 60% is used assuming that 40% of total alkalies from the cement is incorporated in cement hydrates, and not leached out in the hot water extraction method. For instance, a concrete made with 275 kg/m^3 cement containing 1.0% Na_2O_e should contain, after hydration, about 1.65 kg/m^3 water-soluble Na_2O_e (= 275 × 1.0% × 60%). Such a value was used by default for most dams investigated because the cement content and the alkali content of the cement used were generally unknown.

3. Results and discussion

3.1. Tests on aggregate particles

The amounts of Na_2O and K_2O released by the aggregates in each test solution are presented in Fig. 1 as a function of time. The results for quartzite are not illustrated because the values are very low. Table 2 presents the corresponding results obtained after 578 days. Due to the precipitation of siliceous gels after acidification, a number of NaOH and KOH test solutions have not been analysed at ages later than 11 months (greywacke, quartzite), even sometimes 4 months (tuff, Potsdam, Sudbury, Canada), such as the results obtained for these aggregates corresponding to minimum values.

3.1.1. Rate of alkali release and influence of extraction solution

The rates of alkali release always tend to decrease progressively with time, but most aggregates tested are still releasing alkalies after 578 days in each test solution. Most aggregates released less alkalies in lime solution than in alkaline solutions, which are much more aggressive as mentioned above. On average, the soluble Na_2O_e contents at the end of the tests were 0.036%, 0.042%, and 0.117% by mass of aggregate, in water, saturated lime solution, and alkaline solutions, respectively. For a few aggregates, the alkali release was higher in water than in lime solution. This could be attributed to chemical reactions between $Ca(OH)_2$ and some mineral phases within the aggregate particles, which can produce hydrated calcium–aluminum–silicates (CASH), calcium–silicates (CSH), and calcium–aluminates (CAH) [4,24], phases which likely entrap some alkalies.

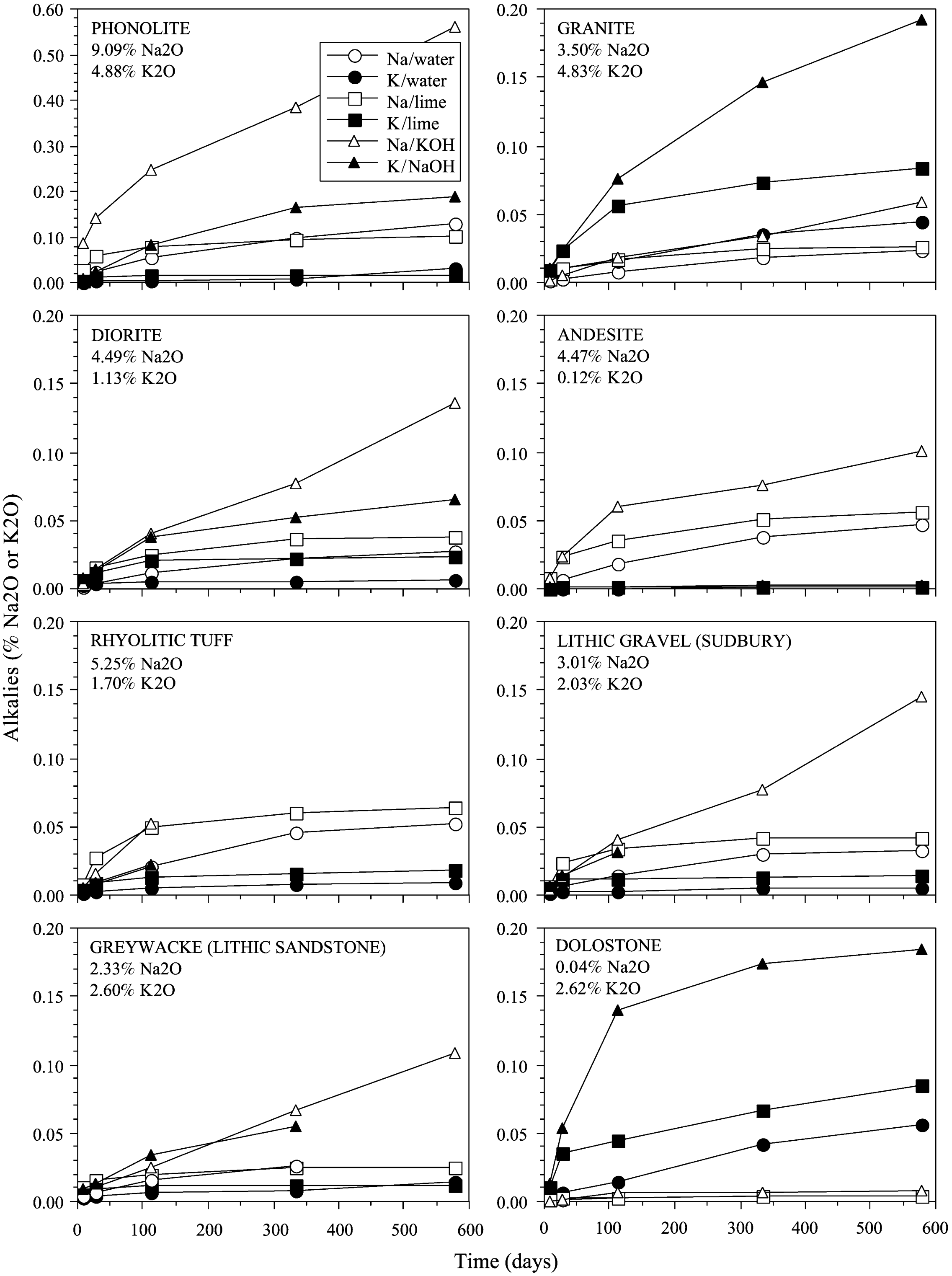

Fig. 1. Alkalies released with time by the aggregates (%Na_2O_e).

3.1.2. Potential alkali contributions to concrete and influence of aggregate type

Based on the maximum values obtained after 578 days in water, lime solution, or alkaline solutions, and on a total aggregate content of 1850 kg/m^3, the amounts of alkalies that could be supplied to the concrete pore water by the aggregates, in the very long term, vary from < 0.1 to 12.7 kg/m^3 Na_2O_e, for an average of 2.2 kg/m^3 (see Table 2). The maximum and average values decrease to 3.4 and 1.6 kg/m^3 Na_2O_e when excluding the highest value obtained for the

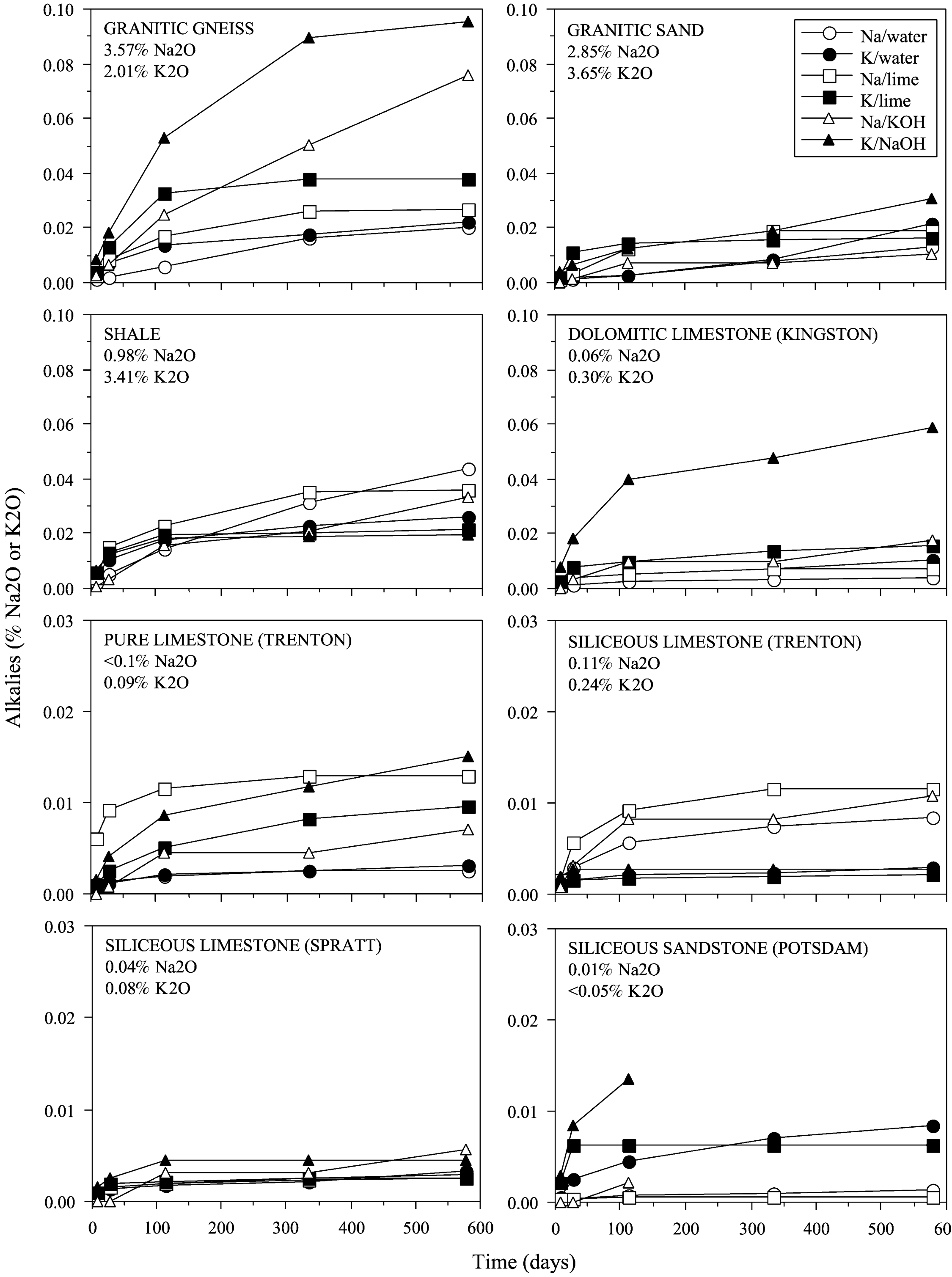

Fig. 1. (*continued*)

nepheline-rich phonolite. This average amount is very important and of the same order of magnitude as the soluble alkali supply by the cement (i.e., about 60% of total alkalies).

Except for the dolostone (2.4 kg/m^3 Na$_2$O$_e$) and the lithic sandstone or greywacke (>2.7), which contain significant amounts of detrital feldspar grains, the aggregates from sedimentary origin (shale: 1.1; dolomitic limestone: 1.1; limestones: 0.4, 0.3, and 0.2; siliceous sandstone: >0.2) released significantly less alkalies than feldspar-rich aggregates from magmatic or metamorphic origin (granite: 3.4; diorite: 3.3; granitic gneiss: 2.6; andesite: 1.9; rhyolitic tuff: >1.5; lithic gravel: >3.1), and particularly those containing also nepheline (phonolite: 12.7). The lowest value ($\approx$0.1 kg/m^3 Na$_2$O$_e$) was for the pure metamorphic quartzite. The granitic sand (0.7 kg/m^3 Na$_2$O$_e$) clearly departs from the feldspar-rich group of aggregates. This fine aggregate is the only one that was not crushed before being tested (natural particles of 1.25–5 mm in size), thus suggesting that aggregate particles exposed for thousands of years in a natural deposit of sand or gravel may have released most of their available alkalies, provided they are not crushed when used in concrete.

The maximum amounts of Na$_2$O$_e$ released after 578 days represent between 1% and 26% of the total alkali content of the aggregates, for an average of 7% (Table 2). However, despite the above remark concerning the feldspar- or nepheline-rich aggregates, there is no clear correlation between the total and the soluble alkali contents of the aggregates tested, as also observed by Van Aardt and Visser [4].

3.1.3. Discussion

The above results, which may appear unrealistic at first, apply to the experimental conditions used in this study, e.g., for particles of 1.25–5 mm in size, using 0.7 M alkaline solutions for extraction, at 38 °C, and with the particle continuously in movement and unconfined (e.g., not embedded in a cement paste), which may have caused particle disaggregation. One may expect higher values for crushed concrete sands, while lower values should apply to aggregates used in concrete at a coarser size, to aggregates that are not crushed such as natural gravels (alkalies already leached), to concretes with less aggressive pore solution (e.g., made with a low alkali cement, a high water/cement ratio, or SCMs), and to concretes exposed to temperature lower than 38 °C. However, the temperature in real concrete may be relatively high for a long period of time, particularly in mass concrete. Moreover, as mentioned before, 0.7 M alkaline solutions are quite similar to the pore solution in many concretes, and the particle size tested is just at the limit between the coarse (5–20 mm) and the fine (0.08–5 mm) aggregates used in concretes. Regarding particle size, more recent experiments performed at Laval University on a number of limestone aggregates indicated that, despite a specific surface area that is four times higher, 0.63–1.25 mm aggregate particles just released about 15–20% more alkalies after 3 months than 1.25–5 mm samples, which suggests that alkalies, under the experimental conditions used, are relatively easy to remove from the interior of the particles, at least for particles smaller than 5 mm (likely because of particle disaggregation). Also, field concrete must usually resist for at least 50 years, which could counterbalance the shorter period of 1.5 years under the more severe test conditions used in this study (e.g., no confinement and continuous agitation).

3.2. Tests on concrete cores

The results obtained for the concrete cores are shown in Table 3 and Figs. 2 and 3. For each concrete element for which measurements were made at different depths, the result in Table 3 is the average of all measurements excluding the surface samples, but all results are shown in Fig. 3. All other measurements were performed on core samples taken at a minimum depth of 0.25 m, except for Samples 11, 16, and 18 from the Rivières-des-Prairies dam, which come from the surface.

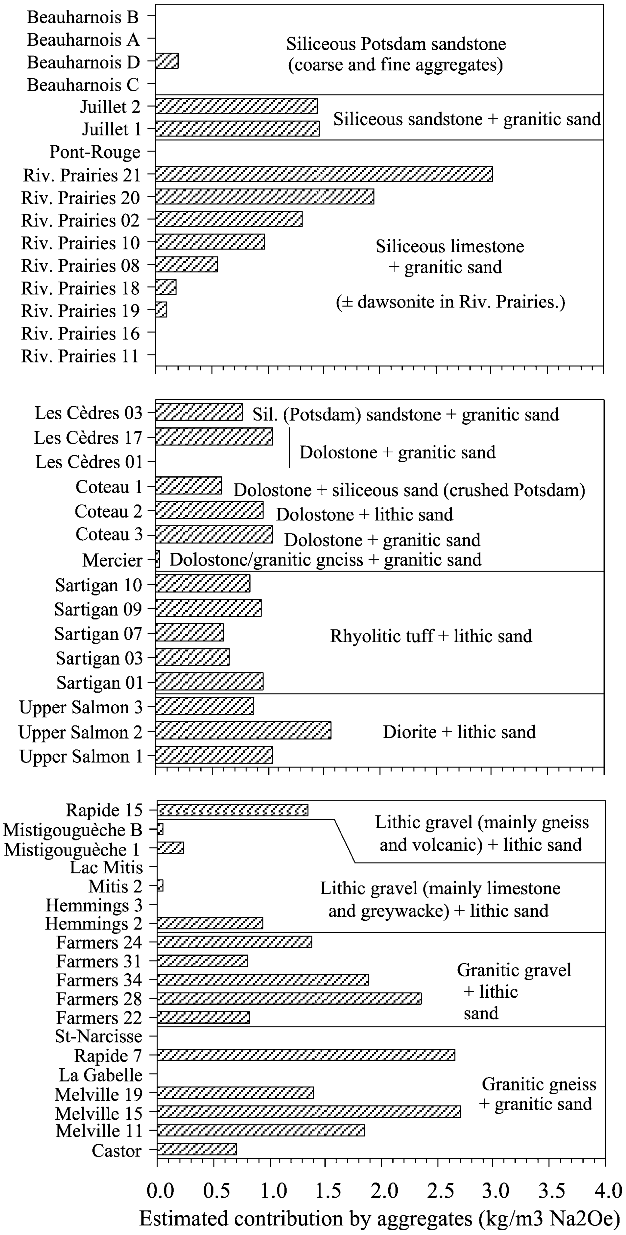

Fig. 2. Estimated alkali contribution by aggregates to the pore solution of mass concrete elements belonging to hydraulic structures.

3.2.1. Causes of discrepancy between measured and expected alkali contents

Before any discussion, it must be mentioned that a measured soluble alkali content lower than the expected soluble alkali content supplied by the cement after hydration, which results in an apparent negative contribution by

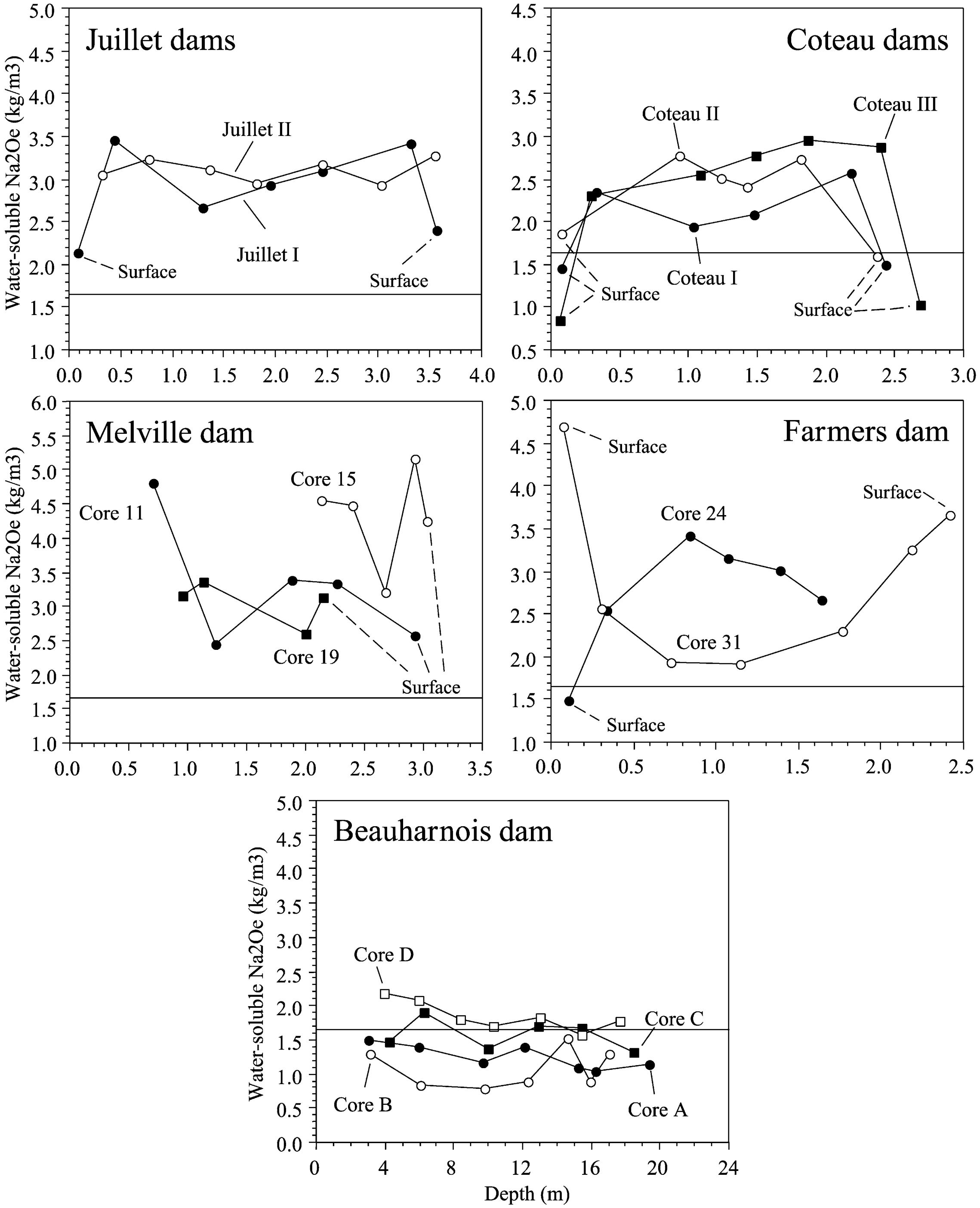

Fig. 3. Water-soluble alkali profiles in mass concrete elements belonging to hydraulic structures.

the aggregates, can be explained by one or more of the following reasons:

(1) Overestimation of the cement dosage, the alkali content in the cement, and/or the above proportion (i.e., 60%) of total alkalies from the cement, which were not incorporated in cement hydrates.

(2) Some alkalies were, and remained at least in part, incorporated in the products from ASR, if present; this was recently demonstrated by Bérubé et al. [21].

(3) Some alkalies migrated out or were leached out of the sampling zone by rain or running water; however, such a leaching should be restricted to the near-surface layer of concrete.

(4) Overestimation of the contribution by aggregates in the test method, which is subtracted from the results.

On the other hand, a measured soluble alkali content greater than the expected soluble alkali content supplied by the cement after hydration, which results in an apparent positive contribution by the aggregates, can be related to one or more of the following factors.

(1) Underestimation of the cement dosage, the alkali content in the cement, and/or the above proportion (i.e., 60%) of total alkalies from the cement, which were not incorporated in cement hydrates. However, it is unlikely that, for most hydraulic structures investigated, cement contents over 275 kg/m^3 and cement with more than 1.0% Na_2O_e were used (estimated values used by default).

(2) Alkali contribution by the aggregates since the concrete was built, which is the principal concern of this study.

(3) Alkali contribution by other concrete constituents, e.g., mixture water, chemical admixtures, and SCMs. However, all mass concretes investigated did not incorporate SCM, chemical admixtures, or mixture water with significant amount of alkalies.

(4) Alkali contribution by external sources, e.g., sea water, brines, and deicing salt. As for leaching, external alkalies should just affect the near-surface layer of the sampled concrete elements. However, all structures investigated were not subjected to external sources of alkalies.

(5) Alkali migration from outside with concentration in the sampling zone, for instance in the near-surface concrete, through evaporation. However, alkali migration and concentration at depth in concrete are doubtful and constitute another concern of this study.

(6) Underestimation of the contribution by aggregates in the test method.

3.2.2. Potential alkali contribution by aggregates and influence of aggregate type

Based on the above discussion, the results obtained as regards the estimated alkali contribution by aggregates from one concrete element to another should be analyzed with circumspection; however, the average behaviors are more significant. As shown in Fig. 2, about 80% (39 among 50) of all concrete elements investigated contains more soluble alkalies than expected from the cement after hydration, thus suggesting that aggregates released alkalies in the concrete pore solution, often more than 1.0 kg/m^3 Na_2O_e (18 times among 50). In many cases, the corresponding concretes were made with crushed alkali-rich aggregates (granitic gneiss, diorite, rhyolitic tuff, Beekmantown dolostone, crushed gravel), which also released high amounts of alkalies in the extraction tests on aggregates.

Very large differences are observed in the soluble alkali content from one concrete element to another of the Rivières-des-Prairies dam. The negative (in fact expressed as 0) or very low values for Elements 11, 16, and 18 can be explained by the fact that the corresponding samples came from the concrete surface (alkali leaching by rain or running water); on the other hand, variable amounts of volcanic rock particles containing water-soluble dawsonite ($NaAl(CO_3)(OH)_2$) were observed in the cores from this dam [25], which thus released variable amounts of alkalies in the concrete pore solution, over 3 kg/m^3 Na_2O_e in one case (Element 21). This rare mineral is found in volcanic silicocarbonatite dykes and sills in some limestone and dolostone quarries in the Montréal area [13]. In order to confirm the above, aggregates were extracted from concrete cores taken in the Rivières-des-Prairies dam, using the freezing in liquid nitrogen/thawing in microwave extraction procedure described by Grattan-Bellew and Danay [12] and Bérubé et al. [26]. After only 7 days *in water*, they released very significant amounts of alkalies, thus confirming that they still contained residual dawsonite.

The alkali contribution by aggregates appears negligible in the case of the concrete elements from the Beauharnois dam, which contain coarse and fine aggregates made of Potsdam siliceous sandstone; this rock was found to release just small amounts of alkalies in the extraction tests on aggregates (see Table 2). On the other hand, some concrete elements (Juillet I, Juillet II, Les Cèdres 3) contain abnormally high amounts of soluble alkalies despite the fact that they contain Potsdam sandstone as coarse aggregates in combination with a granitic sand, which both released before small amounts of alkalies (see Table 2). It must be recalled that the granitic sand tested before was departing from all other feldspar-rich aggregates tested, which all released significant amounts of alkalies (Table 2). This particular result was then assumed to be related to the fact that this aggregate was the only one not crushed for the tests (see Section 3.1). The results obtained for the concrete elements made with a natural gravel and a natural sand, or with the Potsdam sandstone in combination with a natural sand, rather suggest that natural aggregates may supply from very low to high amounts of alkalies to concrete, likely depending upon the conditions to which the deposit was subjected in the field since it was formed.

3.2.3. Alkali migration and concentration in concrete elements

The results obtained for the core samples taken at different depths in a number of concrete elements are shown in Fig. 3. In most cases, one can observe quite large variations with depth in the water-soluble alkali content. Such variations are without obvious trends in the case of the *Melville* dam but present some trends in the other cases. Globally, the soluble alkali content tends to slightly decrease from the top to the bottom of the vertical drillholes made in the plots of the *Beauharnois* dam. This may be attributed to the fact that the average yearly temperature is slightly higher at depth in concrete, which accelerates ASR, then reduces more rapidly the amount of alkali ions in the pore solution.

It is interesting to note that the soluble alkali content of all samples taken at the surface of the two *Juillet* and three *Coteau* dams is significantly lower than the one of the other samples taken at depth. This strongly suggests that significant amounts of alkalies in the near-surface concrete have been leached out by rain or running water since the construction of these dams. Another observation concerning these five dams concerns the fact that the alkali content in about the central part of the sampled pillars is often (four times of five) a little lower than on each side. According to Hydro Québec, in the Montréal area where these dams are located, massive concrete elements are frozen during winter in about the first meter from the exposed surface, while the concrete at greater depth does not freeze, thus allowing ASR to take place all year. Again, a more advanced degree of ASR could explain why the soluble alkali content is a little lower in the central part of these massive pillars.

The case of the *Farmers* dam is also of interest; the same behavior is observed for the Pillar 14 (Core 24), i.e., lower soluble alkali content in the near-surface sample, but Pillar 5 (Core 31) shows the reverse. Concentration by evaporation may explain the increase in the near-surface concrete of this element, which is not exposed to rain neither to running water, thus being protected against alkali leaching. It must be mentioned that the above variations with depth due to alkali leaching by water or precipitation through evaporation appear more important for the Farmers dam than for the Juillet and Coteau dams; the Farmers dam (built in 1926–1929) is not significantly older than the Juillet (1941) and Coteau (1933–1943) dams, but could have been made with a more permeable concrete.

4. Conclusion and recommendation

4.1. Alkali contribution by aggregates

Based on the results obtained from tests on aggregate particles, very significant amounts of alkalies can be supplied with time by aggregates to the concrete pore solution, particularly by feldspar-rich ones (granite, etc.), which are largely used in concrete. After 1.5 years, the amounts of alkalies released by the aggregates in 0.7 M alkaline solutions, which are close to the pore solution in normal concrete, were significantly higher than in water or lime-saturated solution, even when using a solid excess of lime. Based on an aggregate content of 1850 kg/m^3, they vary from one aggregate to another, from < 0.1 to 12.7 kg/m^3 Na_2O_e, for an average of 2.2 kg/m^3, being particularly high for the nephelinitic aggregate tested (phonolite).

The water-soluble alkali content of mass concrete elements from many hydraulic structures was measured using the hot water extraction method, sometimes on many samples taken at different depths inside these elements. Despite a correction being made to take account of the contribution by aggregates in the test method, the results obtained, even at depth in concrete, often largely exceed the water-soluble alkali content expected to be released by the cement, after hydration, often by more than 1.0 kg/m^3 Na_2O_e. This confirms that significant amounts of alkalies can be released with time by aggregates, particularly feldspar-rich ones, as suggested above.

4.2. Procedure for determining the potential alkali contribution by aggregates

It is clear from the above that such a contribution must be considered when designing new concrete structures incorporating reactive aggregates, which calls in turn for a reliable method for determining this contribution. In this respect, short-term immersion tests in a lime-saturated solution are thought to provide values that are greatly underestimated, while long-term immersion tests in NaOH (K release) and KOH (Na release) solutions, as those performed in this study, appear more realistic based on the results obtained for the field concretes.

4.3. Alkali variations inside concrete elements and core sampling

The soluble alkali content in the near-surface concrete, let us say from the surface down to about 0.5 m or less, is often significantly lower and sometimes higher than at depth, which can be related to the conditions to which the concrete elements are subjected in the field (leaching by rain or running water, or precipitation near surface through evaporation). For a better representativeness, it is then recommended to always perform measurements on concrete samples taken at a minimum depth of about 0.5 m or more inside the concrete element under study. Indeed, there is no clear indication that alkalies can migrate and locally concentrate at depth in massive concrete elements; however, a slightly higher yearly temperature may result in a more advanced degree of ASR in the central part of such elements than on each side, then resulting in soluble alkali contents slightly lower than on each side, since more reaction products were formed in which more alkalies are incorporated.

4.4. Design of new concrete structures

In the absence of a more reliable procedure to evaluate the alkali contribution of aggregates to concrete, it is suggested to consider the above results for the design of concrete structures incorporating reactive aggregates, keeping in mind that different varieties of the same type of aggregate may release more or less alkalies, for instance the limestone aggregates used in the Rivière-des-Prairies dam, as mentioned above, which contain various amounts of volcanic particles containing a rare water-soluble alkali mineral called dawsonite.

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References

[1] B. Fournier, M.-A. Bérubé, C.A. Rogers, Proposed guidelines for the prevention of alkali–aggregate reactivity in new concrete structures, Transp. Res. Rec. 1668 (1999) 48–53.

[2] B. Fournier, M.-A. Bérubé, C.A. Rogers, CSA standard practice to evaluate potential alkali-reactivity of aggregates and to select preventive measures against AAR in new concrete structures, in: M.-A. Bérubé, B. Fournier, B. Durand (Eds.), Alkali–Aggregate Reaction in Concrete, 11th International Conference, Laval University, Québec City, 2000, pp. 633–642.

[3] M.-A. Bérubé, J.F. Dorion, D. Vézina, Laboratory and field investigations of the influence of sodium chloride on alkali–silica reactivity, Cem. Concr. Res. (2000) (submitted).

[4] J.H.P. Van Aardt, S. Visser, Calcium hydroxide attack on feldspars and clays: Possible relevance to cement–aggregate reactions, Cem. Concr. Res. 7 (1977) 643–648.

[5] D. Stark, Alkali–aggregate reactivity in the Rocky Mountain region, in: S. Diamond (Ed.), Proceedings of the 4th International Conference on AAR, Purdue, 1978, pp. 235–244 (Publ. No. CE-MAT-1-78).

[6] P.E. Grattan-Bellew, J.J. Beaudouin, Effect of phlogopite mica on alkali–aggregate expansion in concrete, Cem. Concr. Res. 10 (1980) 789–797.

[7] D. Stark, M.S. Bhatty, Alkali–silica reactivity: Effect of alkali in aggregate on expansion, Alkalies in Concrete, ASTM Spec. Tech. Publ., vol. 930, 1986, pp. 16–30.

[8] Y. Mizumoto, K. Kosa, K. Ono, K. Nakano, Study of cracking damage of a concrete structure due to alkali–silica reaction, in: P.E. Grattan-Bellew (Ed.), Concrete Alkali–Aggregate Reaction, Noyes Publications, New York, 1987, pp. 204–209.

[9] H.C. Visvesvaraya, A.K. Mullick, G. Samuel, S.K. Sinha, R.C. Wason, Alkali reactivity of granitic rock aggregates, Proceedings of the 8th Congress on Chemical Cements, 1986, p. 208.

[10] P. Bonnet, Gonflement du béton de plusieurs barrages, Proc. Journées d'Étude sur les Réactions Liants—Granulats dans les Bétons, École Nationale des Ponts et Chaussées, Paris, 1989 (54 pp.).

[11] M. Kawamura, M. Koike, K. Nakano, Release of alkalies from reactive andesitic aggregates and fly ashes into pore solution in mortars, in: K. Okada, S. Nishibayashi, M. Kawamura (Eds.), Proceedings of the 8th International Conference on AAR, Society of Materials Science, Kyoto, 1989, pp. 271–278.

[12] P.E. Grattan-Bellew, A. Danay, Comparison of laboratory and field evaluation of alkali–silica reaction in large dams, Proceedings of the International Conference on AAR in Hydroelectric Plants and Dams, Canadian Electrical Association, Montréal, 1992 (23 pp.).

[13] J.E. Gillott, C.A. Rogers, Alkali–aggegate reaction and internal release of alkalis, Mag. Concr. Res. 46 (1994) 99–112.

[14] M.-A. Bérubé, M. Pigeon, N. Dupont, J. Frenette, M. Langlois, Expan-sion Test Methods for Mass Concrete Exposed to Alkali–Aggregate Reaction, Canadian Electrical Association, Montréal, 1992 (99 pp. plus Appendices; Project CEA No. 715 G 687).

[15] LCPC (Laboratoire Central des Ponts et Chaussées), Essai de granulat — détermination des alcalins solubles dans l'eau de chaux, Méthode d'essai no. 37, Paris, 1993.

[16] S. Diamond, ASR—another look at mechanisms, in: K. Okada, S. Nishibayashi, M. Kawamura (Eds.), Proceedings of the 8th International Conference on AAR, Kyoto, Society of Materials Science, Kyoto, 1989, pp. 83–94.

[17] P.J. Nixon, R.J. Collins, P.L. Rayment, Concentration of alkalies by moisture migration in concrete—a factor influencing alkali–aggregate reaction, Cem. Concr. Res. 9 (1979) 417–423.

[18] P.J. Nixon, I.P. Gillson, An investigation into alkali–silica reaction in concrete bases at an electricity substation at Drakelow power station, England, in: P.E. Grattan-Bellew (Ed.), Concrete Alkali–Aggregate Reaction, Noyes Publications, New York, 1987, pp. 173–177.

[19] D. Stark, Alkali–silica reactivity—some reconsiderations, Cem., Concr., Aggregates 2 (1980) 92–100.

[20] C.A. Rogers, R.D. Hooton, Reduction in mortar and concrete expansion with reactive aggregates due to alkali leaching, Cem., Concr., Aggregates 13 (1993) 42–49.

[21] M.-A. Bérubé, J. Frenette, M. Rivest, D. Vézina, Measurement of the alkali content of concrete using hot-water extraction, in: M.-A. Fournier, B. Fournier, B. Durand (Eds.), Alkali–Aggregate Reaction in Concrete—11th International Conference Proceedings, Laval University, Québec City, 2000, pp. 159–168.

[22] H.F.M. Taylor, Cement Chemistry, Academic Press, London, 1990.

[23] J. Duchesne, M.-A. Bérubé, Effect of supplementary cementing materials on the composition of cement hydration products, Adv. Cem. Based Mater. 2 (2) (1994) 1–10.

[24] M.-A. Bérubé, M. Choquette, J. Locat, Effects of lime on common rock and soil forming minerals, Appl. Clay Sci. 5 (1990) 145–164.

[25] M.-A. Bérubé, A. Pedneault, D. Chouinard, J. Duchesne, J. Frenette, Évaluation, gérance, protection et réparation des ouvrages de béton affectés de réactivité alcalis–silice, Projets R1, R2 et R3, Final report 1993–1996 submitted to Hydro-Québec, 1996, 68 pp.

[26] M.-A. Bérubé, J. Frenette, A. Pedneault, M. Rivest, Laboratory assessment of the potential rate of ASR expansion of field concrete, Cem., Concr., Aggregates 24 (1), in press.