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Alkali mass balance during the accelerated concrete prism test for alkali–aggregate reactivity

Patrice Rivard[a,b,*], Marc-André Bérubé[c], Jean-Pierre Ollivier[b], Gérard Ballivy[a]

[a]Département de génie civil, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1
[b]Laboratoire Matériaux et Durabilité des Constructions, INSA-UPS, Toulouse, 31077, France
[c]Département de géologie et de génie géologique, Université Laval, Sainte-Foy, Quebec, Canada G1K 7P4

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Abstract

The alkali mass balance was calculated in concrete specimens submitted to the storage conditions of the Canadian standard CSA A23.2-14A concrete prism test for expansion due to alkali–aggregate reaction (AAR). The alkali concentration of both the concrete pore solution expressed under high pressure and the water below specimens in storage pails (bottom water) was measured. Measurements were conducted over a 1-year period, which corresponds to the length of the above test. Two reactive aggregates were tested [Potsdam sandstone (PO) and Spratt limestone (SP)]. Each aggregate was incorporated in two concrete mixtures (*mass* concrete and *structural* concrete), for a total of four batches. Significant alkali leaching occurred at 38 °C while performing tests in high moisture storage conditions even though prisms were covered with plastic sleeves. After 52 weeks, the alkali loss ranged from 12% to 25% of the original Na_2O_e content of the concrete, depending on the mixture proportioning and the aggregate type. After estimation of the proportion of alkalis fixed in cement hydrates, it appears that about 23% to 39% of the original alkalis released by the cement are quickly sorbed on aggregate surfaces or have rapidly migrated inside aggregate particles, which may have been incorporated with time in the AAR product. After 52 weeks at 38 °C, the pore solution alkalinity expressed from mass concrete made with PO was 250 mmol/l, whereas the alkalinity was 270 mmol/l in mass concrete incorporating SP. Since prisms of both mixtures were still expanding at 1 year, these alkalinity values are above the thresholds required for sustaining AAR in these concrete mixtures.

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1. Introduction

The method currently used in North America to assess the alkali–aggregate reaction (AAR) is to conduct the Canadian CSA A23.2-14A or the American ASTM C1293 concrete prism test. Since concrete specimens are kept at 38 °C in high moisture conditions (>95% RH). However, these conditions may lead to an underestimation of the ultimate expansion level due to AAR due to the leaching of alkalis. Rogers and Hooton [1] demonstrated that higher expansions are measured when mortar bars were stored in containers without wicks or sealed in polyethylene bags. However, when excessive condensation of water takes place on the specimen surfaces, alkalis are removed from the concrete and the rates of reaction and expansion are reduced. Poole et al. [2] reported that the alkali concentration of both reactive and nonreactive concrete specimens dropped in a similar way after 6 months in high humidity storage conditions. Famy et al. [3] estimated that more than 80% of the alkalis present in pore solution of mortar specimens kept at 90 °C in humid air (90–100% RH) were leached out. Rogers and Hooton [1] measured the residual water-soluble alkali content of concrete prisms using a hot water extraction method after 130 weeks of expansion testing. The authors reported that the residual soluble alkali content dropped 22% for specimens kept at 23 °C in plastic bags with 100 ml of water while this value reached 63% for specimens stored in humid room at the same temperature. When stored over water in a sealed box at 38 °C, a change in the residual water-soluble alkali content of − 42% was measured. However, it must be

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* Corresponding author. Département de génie civil, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1. Tel.: +1-819-821-8000x3378; fax: +1-819-821-7974.

E-mail address: Patrice.Rivard@USherbrooke.ca (P. Rivard).

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Table 1
Concrete mixture proportioning

	PO-mass	PO-structural	SP-mass	SP-structural
Cement content (kg/m^3)	320	420	320	420
Coarse aggregates (kg/m^3)	1097	1063	1142	1113
Fine aggregates (kg/m^3)	762	739	741	742
Water (kg/m^3)	175	167	176	168
w/c	0.55	0.40	0.55	0.40
Total alkalis (kg/m^3 Na_2O_e)	4.00	5.25	4.00	5.25

pointed out that the depletion of alkali content in concrete cannot be exclusively attributed to leaching because AAR consumes some alkalis by incorporation into reaction gels [4].

Several other studies showed that greater expansions are measured in the long term for mortar or concrete specimens of larger cross-section, which is attributed to lesser alkali leaching [5–10]. Wrapping concrete specimens or simply covering them with plastic sleeves seems to reduce the alkali loss, which leads to higher expansion levels [1,4,11].

The aim of the work presented here is to evaluate, over a 1-year period, the alkali mass balance in concrete affected by alkali–silica reaction in an open system kept at 38 °C. The alkali composition of the pore solution, the alkali loss by leaching, and the water gain of specimens undergoing microcracking were all measured and taken into account in the calculations.

2. Experimental

Two reactive Canadian crushed aggregates were selected for this study, the Potsdam sandstone (PO) and the Spratt limestone (SP). Two concrete mixtures were prepared with each aggregate: the first one, referred to *structural* concrete, was made following the CSA A23.A-14A specifications, and the second one was designed to simulate *mass* concrete as usually found in hydraulic dams (Table 1). Aggregates were brought to SSD prior to batching. A normal ASTM Type I cement was used in the preparation of both mixtures. Cement composition is given in Table 2. Alkali content was raised to 1.25% Na_2O_e of the cement mass by adding NaOH pellets to the mixing water. No other chemical or mineral admixtures were used. All batches were mixed according to the CSA A23.A-14A specifications.

Table 2
Chemical composition of the cement

Element	Content (%)
CaO	62.4
SiO_2	19.6
Al_2O_3	4.28
SO_3	3.74
Fe_2O_3	3.37
MgO	2.03
Na_2O_e	0.82
K_2O	0.95
Na_2O	0.19
TiO_2	0.20

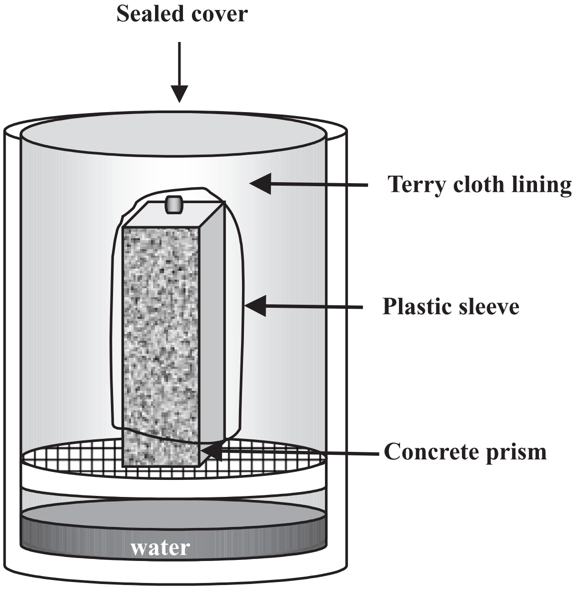

Fig. 1. Storage of concrete specimen in plastic pails.

Four series of concrete prisms (75 × 75 × 300 mm in size) were cast from the four batches. The prisms were demoulded after 24 h and stored in hermetic 25-l plastic pails lined with a damp terry cloth. Four specimens were placed in each pail. The high humidity level was ensured by placing approximately 2 cm of water in the bottom of the pails, which gives about 2200 ml of water. Prisms were placed vertically on a plastic perforated rack at about 5 cm above water level to avoid direct contact (Fig. 1). With the attempt to reduce alkali leaching, the prisms were covered with a plastic sleeve close at the top and loose at the bottom (Fig. 1). The pails were then stored in a heated room at 38 °C. A small volume (± 50 ml) of water at the bottom of different pails was collected at 1, 4, 12, 24, 36, and 52 weeks. Simultaneously, concrete prisms from one pail were broken into chunks and the pore solution was expressed by using a high-pressure apparatus [12]. The extracted pore solution was analyzed by atomic absorption spectroscopy.

3. Results

3.1. Pore solution analysis

Chemical analysis of the pore solution expressed from concrete is given in Table 3. Most of the time, insufficient

Table 3
Alkali concentration in the pore solution of the concrete prisms cured at 38 °C (pore expression via high pressure)

Mixture	Week	Expansion (%)	Pore solution concentration (mmol/l)		
			[Na]	[K]	[Na + K]
PO-mass	1	− 0.002	221	211	432
	4	0.000	135	165	300
	12	0.009	221	187	407
	24	0.059	208	121	329
	36	0.094	190	112	302
	52	0.111	113	139	252
PO-structural	1	0.000	314	367	681
	4	− 0.004	330	478	808
	12	0.015	231	398	629
	24	0.057	–	–	–
	36	0.122	–	–	–
	52	0.150	–	–	–
SP-mass	1	0.000	193	184	377
	4	0.001	209	194	402
	12	0.019	193	112	305
	24	0.109	149	127	276
	36	0.178	124	130	253
	52	0.251	142	126	269
SP-structural	1	0.000	227	177	404
	4	0.006	232	188	419
	12	0.075	–	–	–
	24	0.154	–	–	–
	36	0.188	196	166	362
	52	0.217	–	–	–

amount of liquid was recovered from the structural concrete prisms to enable analysis. The alkali concentration in the Spratt structural concrete at 1 and 4 weeks was lower than expected, being slightly higher than in the Spratt mass mixture. Other analysis performed on a different structural concrete batch made with the SP indicated an alkali concentration of 686 mmol/l at 7 days, which seems more appropriate [12]. The water-to-cement ratio (w/c) was not doubtful since compressive strength results were consistent with previous work.

A general decreasing trend is observed in the pore solution alkali concentration. After 52 weeks, the alkali concentration [Na + K] decreased by 29% for Spratt mass concrete and 42% for Potsdam mass concrete, to reach 269 and 252 mmol/l, respectively.

3.2. Amount of alkalis in bottom water

Chemical analyses of the bottom water in the pails revealed substantial alkali leaching despite the fact that prisms were covered with plastic sleeves (Fig. 2). The amount of alkali leaching for both mass and structural mixtures increases with time. Nevertheless, a plateau seems to be reached before 52 weeks for both structural mixtures, despite ongoing expansion of the concrete specimens (Fig. 3). The results shown in Fig. 2 represent losses for one prism, the measured value being divided by four (four specimens in each pail).

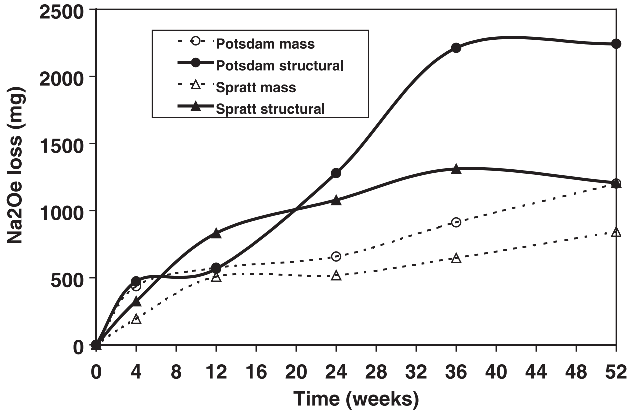

Fig. 2. Alkali leaching for one prism cured at 38 °C (amount of alkalis measured in the bottom water in pails).

Except for the Spratt structural specimens, the three other mixtures followed a similar trend during the first 12 weeks (Fig. 2). At 52 weeks, the Potsdam structural concrete released nearly twice the amount of alkalis as were released by all the Spratt specimens and by the Potsdam mass specimen.

For the same aggregate, the amount and rate of leaching is greater for structural mixtures (Fig. 2). This is related to the higher cement and alkali contents in these mixtures (5.25 kg/m^3 Na_2O_e compared to 4.00 kg/m^3). For the same mixture, concrete alkali leaching seemed to be greater for the Potsdam specimens compared with the Spratt specimens.

The proportion of leached alkalis, regardless of the alkalis fixed into the hydrates or incorporated into the AAR reaction gels, can be estimated from the total alkalis supplied by the cement. The original alkali content in concrete was 5.25 and 4.00 kg/m^3 Na_2O_e for the structural and mass mixtures, respectively. The volume of a single prism is 0.0017 m^3, giving 6.75 g Na_2O_e (mass) and 8.86 g Na_2O_e (structural) per prism. Therefore, the amount of

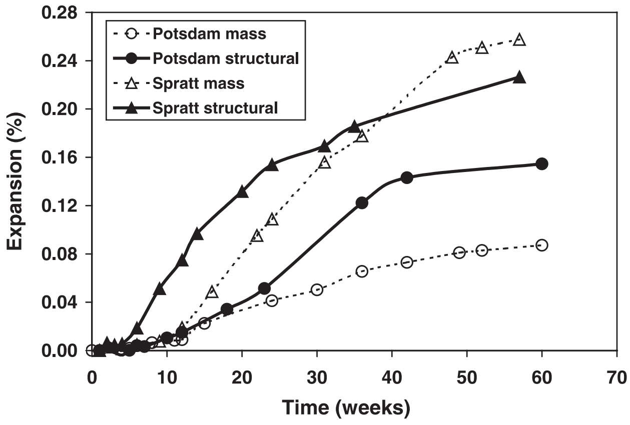

Fig. 3. Average expansion curves for prisms stored over water at 38 °C.

alkalis measured in the bottom water can be converted to percentages of total alkalis. Losses at 52 weeks represent 12% (Spratt mass), 14% (Spratt structural), 18% (Potsdam mass), and 25% (Potsdam structural) of the initial alkali content supplied by cement. Considering the amount of alkalis potentially fixed in the hydrates that cannot be leached out—estimated to be about 42% of the total alkalis for ordinary Portland cement [13,14]—the proportions of leachable alkalis increase to 22% (Spratt mass), 24% (Spratt structural), 30% (Potsdam mass), and 45% (Potsdam structural concrete). The above results suggest that, despite lower porosity and permeability, the structural concrete specimens (as tested in CSA A23.2-14A) are also subjected to intense leaching, even more important than for the mass concrete.

3.3. Alkali mass balance

On the basis of the laboratory results presented above, an alkali mass balance was calculated. Some assumptions had to be made:

1) The degree of hydration at 38 °C is 75%, 90%, and 100% at 1, 4, and 12 weeks, respectively, and unhydrated cement grains have not released their alkalis;
2) OPC hydrates contain about 32% chemically bound water for fully hydrated paste [14];
3) The proportion of total alkalis entrapped in cement hydrates is about 42% [13,14];
4) The chemistry of the expressed solution is representative of the concrete pore solution.

The results of calculations are provided in Table 4. The third column of Table 4 is the mean weight of all test prisms. The fourth column is the residual water in each prism, given by the difference between the mixing water and the water incorporated in hydrates. The fifth column is the amount of free water in one prism, i.e., the residual water + the water gain given by prism mass variations. The following columns are the alkali mass balance in one prism. The summation of these four columns gives the total original alkali content in one prism (6.75 g in mass mixtures and 8.86 g in structural mixtures). The ninth column (*others*) represents the amount required to reach the initial alkali content, which may include alkalis in the products from AAR. More details on calculations are given in other work [12].

According to the assumptions stated above, about one-third of the total alkalis are in solution after 1 week of curing, except for the structural mixture incorporating SP where only a proportion of 18% was calculated (Fig. 4). The proportion of alkalis in solution tends to decrease with time for all mixtures. On the other hand, the proportion of

Table 4
Alkali mass balance in 75 × 75 × 300 mm concrete specimens subjected to the concrete prism test CSA A23.2-14A (38 °C)

Mixture	Week	Prism weight (g)	Water (g)		Na_2O_e (g)			
			Residual water	Pore water	In hydrates	In pore solution	Leached	Others
PO-mass	0	4058	297.0	297.0	0	0	0	6.75
	1	4059	167.4	168.8	2.14	2.26	0.11	2.24
	4	4063	141.5	146.4	2.57	1.36	0.44	2.39
	12	4070	124.2	136.3	2.85	1.72	0.57	1.60
	24	4073	124.2	139.7	2.85	1.43	0.66	1.82
	36	4078	124.2	144.2	2.85	1.35	0.91	1.64
	52	4081	124.2	147.5	2.85	1.15	1.20	1.55
PO-structural	0	4036	297.7	297.7	0	0.00	0	8.86
	1	4037	127.7	128.6	2.81	2.71	0.12	3.22
	4	4039	93.6	96.6	3.37	2.42	0.47	2.60
	12	4046	70.9	80.9	3.74	1.58	0.57	2.97
	24	4042	70.9	76.9	3.74	–	1.28	–
	36	4059	70.9	93.9	3.74	–	2.21	–
	52	4062	70.9	96.9	3.74	–	2.24	–
SP-mass	0	3995	297.0	297.0	0	0.00	0	6.75
	1	3995	167.4	167.6	2.14	1.96	0.05	2.61
	4	3999	141.5	145.5	2.57	1.81	0.19	2.18
	12	4000	124.2	129.2	2.85	1.22	0.51	2.17
	24	4010	124.2	139.2	2.85	1.19	0.52	2.19
	36	4015	124.2	144.2	2.85	1.13	0.65	2.12
	52	4018	124.2	147.2	2.85	1.22	0.84	1.83
SP-structural	0	4040	297.7	297.7	0	0.00	0	8.86
	1	4040	127.7	127.6	2.81	1.60	0.08	4.37
	4	4046	93.6	99.6	3.37	1.30	0.33	3.87
	12	4056	70.9	86.9	3.74	–	1.08	–
	24	4060	70.9	90.9	3.74	–	1.19	–
	36	4064	70.9	94.9	3.74	1.06	1.31	2.74
	52	4068	70.9	98.9	3.74	–	1.21	–

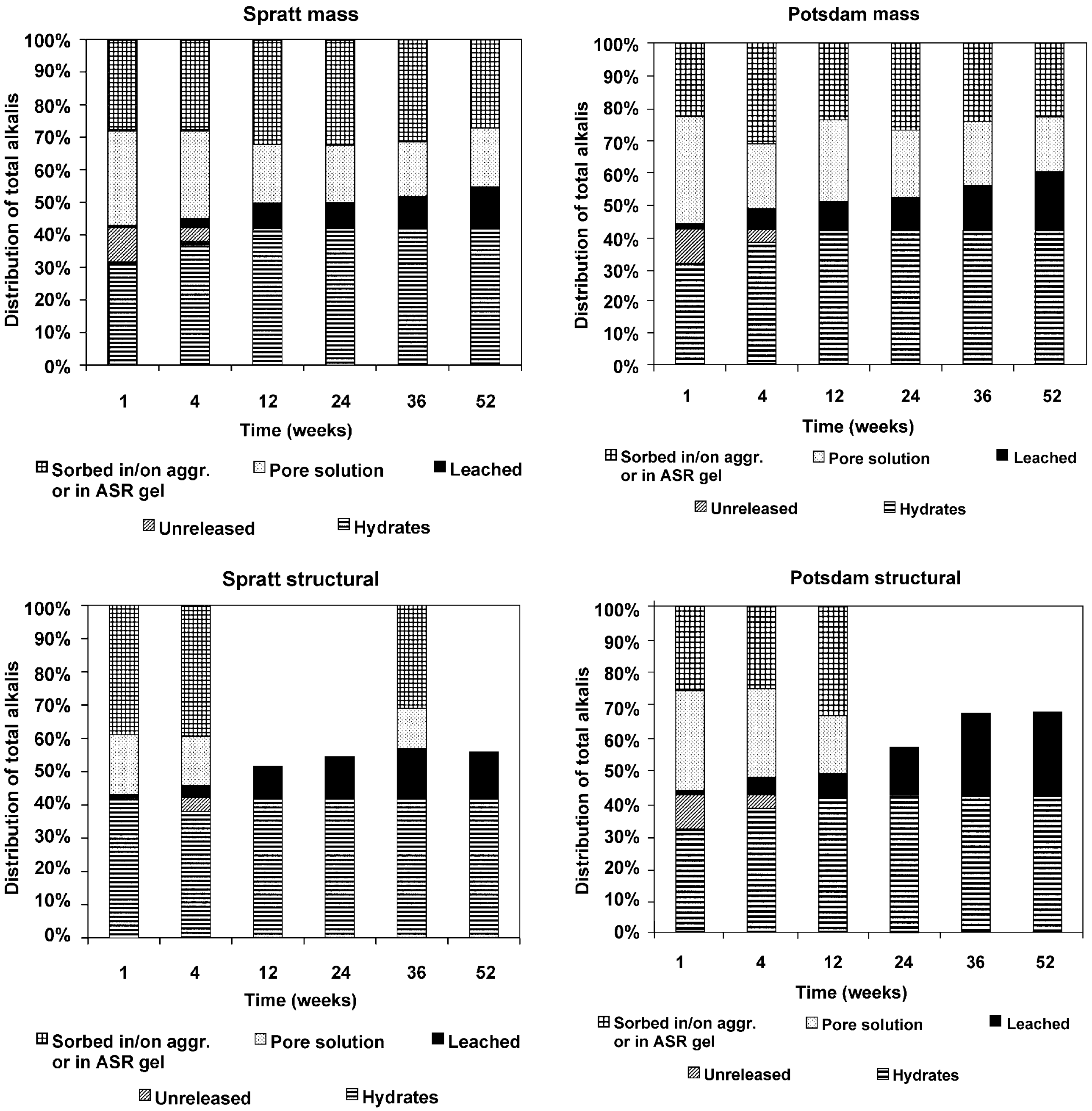

Fig. 4. Alkali mass balance in concrete prisms subjected to the concrete prism test CSA A23.2-14A (38 °C).

leached alkalis, as measured in bottom water, increased with time.

4. Discussion

According to the calculations made at 1 week, 23% of the total alkalis in the Potsdam mass prisms were not incorporated in hydrates neither detected in pore solution nor leached out, whereas this proportion slightly increased to 25% in the Potsdam structural prisms (Fig. 4). These “missing” alkalis are given in the ninth column of Table 4 (others). The proportions of missing alkalis at 1 week were 28% and 39% in the Spratt mass and Spratt structural prisms, respectively. After 12 weeks, the proportions of missing alkalis remained quite constant in all cases (Fig. 4). The lack in alkalis might be explained by alkali sorption phenomena on silica phases of aggregates. At early ages, some alkalis are believed to be sorbed on aggregate external surfaces. A certain amount could even have migrated within aggregate particles. Other work showed significant calcium and alkali concentrations inside Potsdam sandstone particles

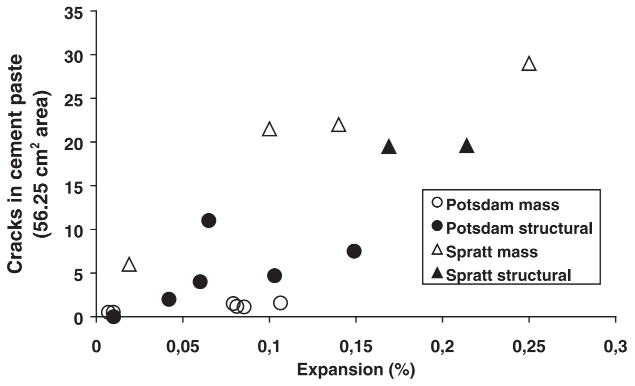

Fig. 5. Number of cracks counted in the cement paste of a 56.25-cm^2 concrete section at × 16 magnification.

of alkali-enriched concrete kept 14 days at 21 °C in a curing room [16]. However, as AAR progresses, silica gels are formed and incorporate alkali ions. Thus, some of these "missing" adsorbed or absorbed alkalis are likely part of AAR-gel structure after a number of weeks.

The crack network stemming from AAR expansion cannot be put forward to explain the difference between the Spratt and Potsdam concretes regarding the amount of leached alkalis. It has been shown that the SP generates more cracks in concrete than the PO [15]. Detailed petrographic examinations conducted during this study confirmed that the degree of cracking is higher in Spratt concrete samples. Fig. 5 shows the number of cracks counted using a stereomicroscope at a magnification of × 16. This may suggest that leaching is not significantly influenced by the thin cracking network that occurs in laboratory test specimens.

The reaction rate certainly has an effect on the rate of alkali consumption, as well as on alkali leaching. The use of the SP aggregate in concrete leads to greater swelling rate and expansion level compared to the PO aggregate. Therefore, more alkalis are incorporated into reaction gels with the SP, and become "unavailable" for subsequent leaching. The reaction is slower with the PO, which allows more alkali to be leached from the pore solution. On the other hand, the PO does not release alkalis that would contribute to greater leaching because this rock is mainly composed of silica (>98%).

It is widely accepted that there is a certain threshold in alkali content for initiating and sustaining AAR in concrete. The "absolute" limit is not well defined and depends largely on the aggregate reactivity [17]. For instance, Duchesne and Bérubé [18] reported a minimum initial level of about 3 kg/m^3 Na_2O_e for two highly reactive aggregates. Recent studies tend to conclude that a limit of about 5 kg/m^3 Na_2O_e seems to be acceptable for low reactivity aggregates [11,19]. This value can be reached quite quickly with intense alkali leaching. Therefore, some low reactivity aggregates might be accepted by accelerated tests where concrete specimens are stored at high humidities. Moreover, long-term expansion could be prematurely stopped due to alkali leaching, as reported by Duchesne and Bérubé [20].

The data presented in this paper should be judged with care because:

- The high-pressure extraction method allowed to recover from 6% to 28% of concrete evaporable water [12];
- The several calculations accumulate experimental errors;
- The mass balance is based on some assumptions.

5. Conclusions

The analysis of concrete pore solution and bottom water enabled the calculation of an alkali mass balance in AAR-affected concrete. Significant leaching occurs when performing accelerated expansion tests in the high moisture environment that prevails in the Canadian CSA A23.2-14 or American ASTM C1293 concrete prism tests, even though test prisms were covered with plastic sleeves. After 52 weeks in high moisture storage, concrete prisms lost from 12% (Spratt mass) to 25% (Potsdam structural) of their initial Na_2O_e content. Mass balance suggest that about 23% to 39% of the original alkalis in the cement were quickly adsorbed on aggregate surfaces or rapidly migrated inside aggregate particles. After 52 weeks, the alkalinity of the pore solution expressed from mass concrete made with the PO was 250 mmol/l, whereas the alkalinity was 270 mmol/l in mass concrete incorporating the SP. Since prisms of both mixtures were still expanding at this age, these alkalinity values are above the thresholds required for sustaining AAR in mass concrete mixtures incorporating these aggregates.

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