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Topics

ALKALI CONTRIBUTION BY AGGREGATES TO CONCRETE

M.A. Bérubé, J. Duchesne
Department of Geology and Geological Engineering
Laval University, Québec City, Québec, Canada, G1K 7P4

M. Rivest
Hydro Québec, 800E Maisonneuve Blvd.,
17th floor, Montréal, Québec, Canada, H2L 4P5

ABSTRACT

Seventeen different concrete aggregates were selected for this study. For each of them, sub-samples of 1.25-5 mm particles were immersed in distilled water (K and Na supplies), lime saturated solution with solid lime in excess (K and Na supplies), 0.7M NaOH (K supply) and 0.7M KOH (Na supply), always at 38°C, and agitated continuously for 578 days. Solution samples were analysed after 7, 28, 112, 335 and 578 days for K and/or Na. The results indicate that the rates of alkali release decrease progressively with time, but most aggregates tested are still releasing alkalies after 578 days in each test solution. Much more alkalies are usually released in alkaline solutions than in lime saturated solution, with lower values in water. After 578 days, the aggregates released between <0.01 to 0.19% Na_2O_{eq}, excluding the highest value obtained for the nephelinitic aggregate tested or phonolite (0.68%). This would correspond to a contribution to concrete of <0.1 up to 3.4 kg/m^3 Na_2O_{eq} (12.7 for the phonolite), based on an aggregate content of 1 850 kg/m^3. In general, the feldspar-rich aggregates released significantly more alkalies than other types.
Keywords: Alkali-aggregate reaction, Aggregates, Alkali contribution, Leaching tests, Alkaline solutions.

INTRODUCTION

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. Moreover, the higher the alkali concentration, the greater the expansion due to AAR usually is. In general, the soluble alkalies are mostly supplied by the cement, but some may also be provided by chemical or mineral additives, by the mixture water (salt), or by secondary sources such as sea-water, deicing salts and industrial brines. 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 (Van Aardt & Visser 1977, Stark 1978, Grattan-Bellew & Beaudouin 1980, Stark & Bhatty 1986, Mizumoto *et al.* 1987, Visvesvaraya *et al.* 1987, Bonnet 1989, Kawamura *et al.* 1989, Grattan-Bellew & Danay 1992, Gillott & Rogers 1994). This could explain why some concrete structures are affected by ASR, although built with low alkali cements (<0.6% Na_2O_{eq}) and/or with cements which supply less than 3 kg/m^3 Na_2O_{eq}, and even less than 2 kg/m^3, as observed by many workers referred to in Bérubé *et al.* (1992).

A number of experimental procedures have been used to estimate the alkali contribution by aggregates to the concrete pore solution (see Table 1). However, the number and types of aggregates 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 period 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, most of time with no solid lime in excess, which is much less agressive than in normal concrete. Indeed, 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_{eq}, for instance, is around 0.7M (pH $\approx$ 13.85) after 28 days (Diamond 1989), which is 34 times more than in a saturated lime solution ([OH]$^-$ $\approx$ 0.021M and pH $\approx$ 12.32 <u>at 38°C</u>), 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.

The objectives of this study were 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 to evaluate these amounts for a wide variety of aggregates from Québec and Ontario (Canada).

Table 1 Procedures used to evaluate the alkali contribution by aggregates.

Test conditions	Van-Aardt & Visser 1977	Stark & Bhatty 1986	Kawamura et al. 1989	LCPC 1991	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)	500g, as used in concrete (but <20 mm)	40 g, 1-5 mm (some tests: 0.63-1 mm)
Extraction solution	0.5 g lime in 25 ml water (lime sat. + excess lime)	1a,1b) 25 ml lime sat. 1c) 25 ml dist. water 2) 500 ml lime sat.	200 ml lime saturated	20 g lime in 300 ml dist. water (lime sat. + excess lime)	40 ml of: • dist. water • lime sat. + excess lime • 0.7N NaOH • 0.7N 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) & 2)	-	-	Yes
Test period	250 d	1a) 7-90 d 1b,1c) 28 d 2) 7-180 d	1-180 d	7 d	7-578 d
% soluble Na_2O_{eq}[1]	0.01-2.32	1a) 0.31-1.99 (10)[2,3] 1b) 0.83-5.03 (4)[2] 1c) 0.03-0.13 (4)[2] 2) 0.07 (1)[2,4]	0.02 & 0.07	-	0.003-0.68

[1]: Maximum values obtained during the test period, (usually at the end), by mass of aggregate.
[2]: Number between brackets corresponds to the number of aggregates tested.
[3]: 0.45-1.99 for the 4 aggregates tested under conditions 1b and 1c.
[4]: The aggregate tested gave 0.45 under condition 1a.

MATERIALS AND METHODS

Seventeen materials 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 size 1.25 to 5 mm.

For each aggregate, 40 g sub-samples of particles of this size were placed in 60-ml capacity Nalgene bottles along with 40 ml of various solutions: (1), distilled water (K and Na supplies); (2), lime saturated solution with an excess of 1 g of solid lime (K and Na supplies); (3), 0.7N NaOH (K supply), and (4), 0.7N KOH (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 hours at room temperature, for particle settling, then 10 ml samples of solution were taken out by pipeting, 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 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 during each period of measurement.

RESULTS AND DISCUSSION

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 later ages than 11 months (greywacke, quartzite), even sometimes 4 months (tuff, Potsdam, Sudbury), such as the results obtained for these aggregates correspond to minimum values.

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 agressive as mentioned above. On average, the soluble Na_2O_{eq} contents at the end of the tests were 0.036%, 0.042% and 0.117%, in water, saturated lime solution and alkaline solutions, respectively, by mass of aggregate. 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) (Bérubé et al. 1990, Van Aardt & Visser 1977), which phases likely entrap some alkalies.

Based on the maximum values obtained after 578 days in water, lime solution or alkaline solutions, and on a total aggregate content of 1 850 kg/m³, 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 up to 12.7 kg/m³ Na_2O_{eq}, for an average of 2.2 kg/m³ (see Table 2). The maximum and average values decrease to 3.4 and 1.6 kg/m³ Na_2O_{eq} if we exclude the highest value obtained for the phonolite. This average amount is very important and of the same order of magnitude as the alkali supply by the cement.

Except for the dolostone (2.4 kg/m³ Na_2O_{eq}) 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 nepheline (phonolite: 12.7). The lowest value ($\approx$0.1 kg/m³ Na_2O_{eq}) was for the pure metamorphic quartzite. The granitic sand (0.7 kg/m³ Na_2O_{eq}) clearly departs from the feldspar-rich group of aggregates. This fine aggregate is the only one that was not crushed for tests, being screened, which may suggest 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.
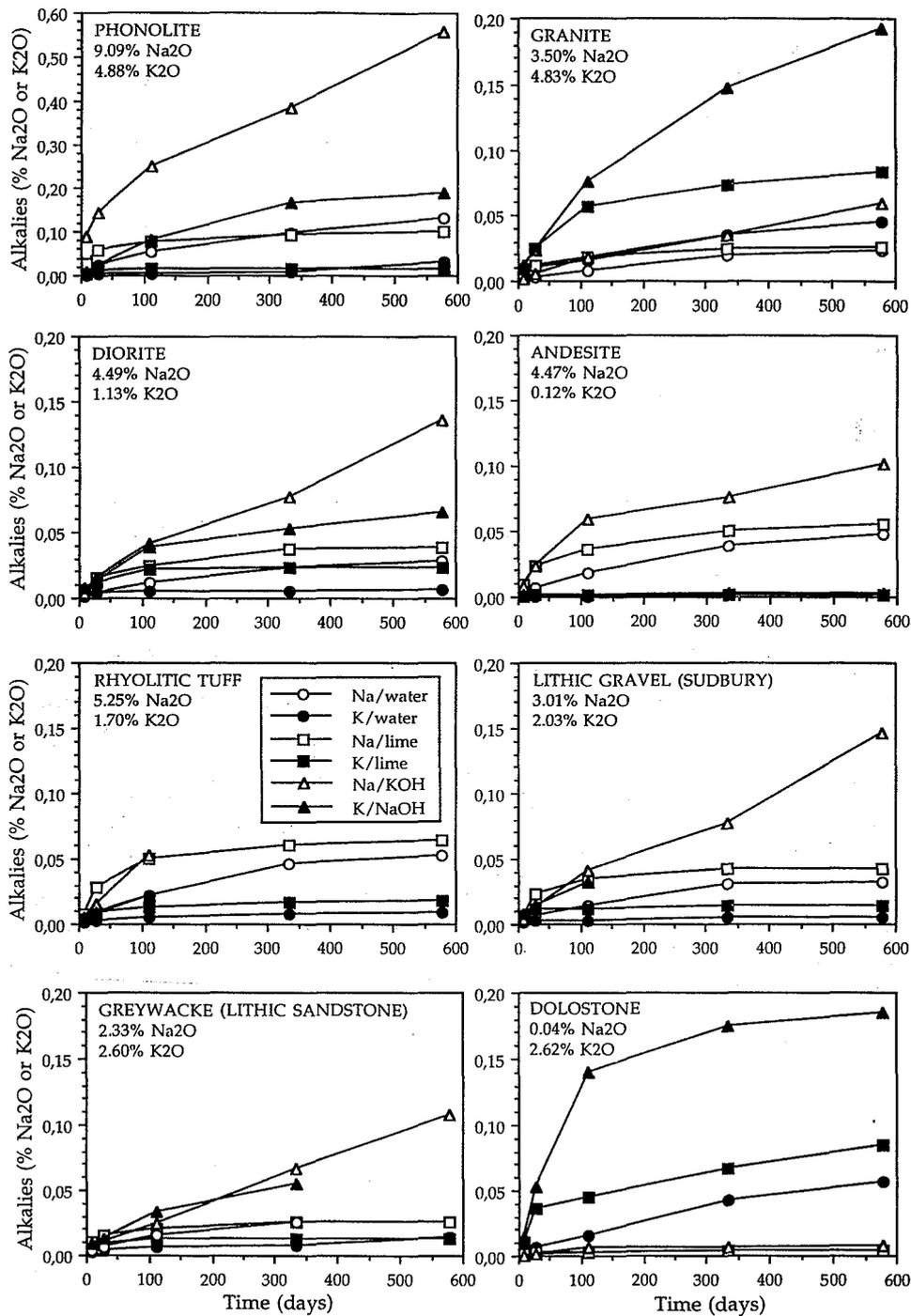
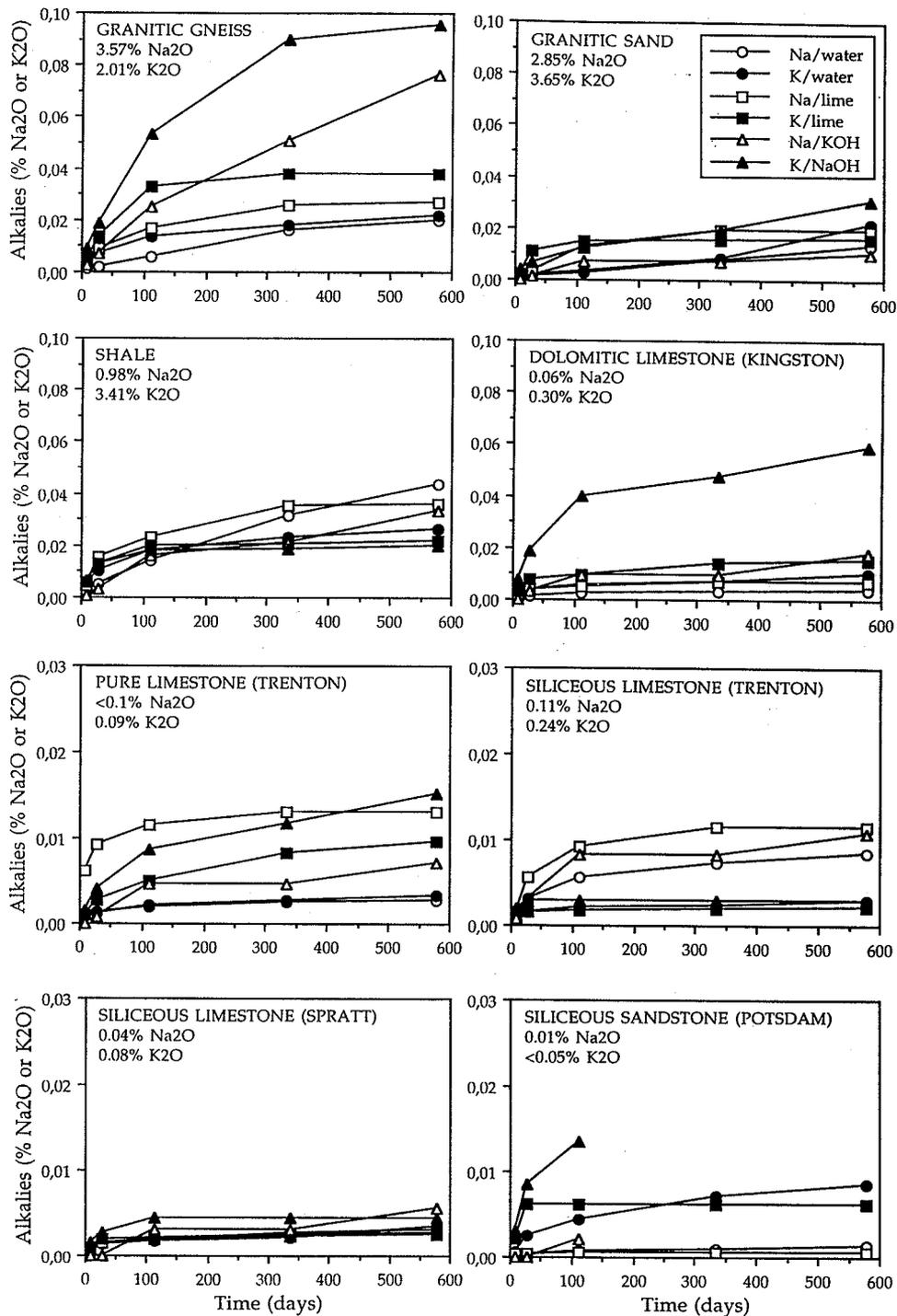Fig. 1 Alkalies released with time by the aggregates (%Na2Oeq).

Fig. 1 (cont'd) Alkalies released with time by the aggregates (%Na₂O_eq).

Fig. 1 (cont'd) Alkalies released with time by the aggregates ($\%Na_2O_{eq}$).

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

Aggregate	--- Total alkalies ---			-- Soluble alkalies --										
				------ Pure water ------			---- Lime solution ----			-- Alkaline solutions --			-- Maximum[1] --	
	Na_2O	K_2O	Na_2O_{eq}	Na_2O	K_2O	Na_2O_{eq}	Na_2O	K_2O	Na_2O_{eq}	Na_2O^2	K_2O^2	Na_2O_{eq}	Na_2O_{eq}	
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%/tot.)[3]	(kg/m³)[4]
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[5]	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)[7]	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	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)[7]	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
Dol. limestone (Kingston)[5]	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
Sil. limestone (Trenton)[6]	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
Sil. limestone (Spratt)[5]	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
Sil. sandstone (Potsdam)[6]	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

[1]: Maximum Na_2O contribution + maximum K_2O contribution in water, lime solution or alkaline solutions, which most of time correspond to alkaline solutions.

[2]: Na_2O contribution measured in 0.7N KOH and K_2O contribution measured in 0.7N 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.

[3]: Percentage of total alkalies (Na_2O_{eq}) in the aggregate.

[4]: Based on a total concrete aggregate content of 1 850 kg/m³.

[5]: Highly reactive aggregate; alkali-silica reactivity except for the dolomitic limestone (alkali-carbonate reactivity).

[6]: Moderately reactive aggregate; alkali-silica reactivity.

[7]: Slowly/marginally reactive aggregate; alkali-silica reactivity.

The maximum amounts of Na_2O_{eq} 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 not a clear correlation between the total and the soluble alkali contents of the aggregates tested, as also observed by Van Aardt & Visser (1977).

CONCLUSION

Based on the results obtained, with time, significant amounts of alkalies can be supplied by aggregates to the concrete pore solution. After 1.5 years, the amounts of alkalies released by the aggregates in 0.7M alkaline solutions, which are close to the pore solution in normal concrete, are significantly higher than in water or lime saturated solution, even when using a solid excess of lime. Based on an aggregate content of 1 850 kg/m^3, they vary from one aggregate to another, from <0.1 up to 12.7 kg/m^3 Na_2O_{eq}, for an average of 2.2 kg/m^3, being particularly high for the nephelinitic aggregate tested (phonolite).

These results apply to the experimental conditions used in this study, e.g. for particles of size 1.25 to 5 mm, using 0.7M alkaline solutions for extraction, at 38°C, and with the particle continuously in movement and unconfined (e.g. not embedded in a cement paste). One may expect higher values for 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, or supplementary cementing materials), and to concretes exposed to low temperature.

However, the temperature in concrete may be relatively high for a long period of time, particularly in mass concrete. Moreover, as mentioned before, 0.7M 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 commonly used in concretes. Regarding particle size, recent experiments performed at Laval University on a number of limestone aggregates indicated that, despite a specific surface area which is four times higher, 0.63-1.25 mm aggregate particles released about 15 to 20% more alkalies after 3 months than 1.25-5 mm samples, which suggest 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. 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 that study (e.g. no confinement and continuous agitation).

It is then suggested to use the above values for the design of concretes incorporating potentially reactive aggregates. One can use the values obtained for the aggregate types which approach in composition the coarse and fine aggregates to be used in the field, keeping in mind that different varieties of the same type of aggregate may release more or less alkalies. The results obtained recently at Laval University for a number of limestone aggregates clearly confirm this remark. These aggregates were extracted from concrete cores taken in different components of a dam in the Montreal area. After only 7 days in water, they released very significant amounts of alkalies, which suggest that they contain water-soluble alkali minerals, likely to be in the form of dawsonite ($NaAl(CO_3)(OH)_2$), a rare mineral found in volcanic silicocarbonatite dykes and sills in some limestone and dolostone quarries in the Montreal area (Gillott & Rogers 1994).

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