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# Validation of the alkali contribution by aggregates to the concrete pore solution

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## ABSTRACT

Mortar and concrete specimens were made with six reactive and non-reactive aggregates from Eastern Canada, with different alkali contents, to determine their alkali contribution to the pore solution. Two methods were used to determine the alkali content of samples over time: the high pressure extraction method and the espresso extraction method. Also, an alkali leaching test was conducted directly on the same aggregate materials. One aggregate was clearly identified as a potential source of $Na^+$ to the pore solution. Results obtained after one year at 60 °C showed that rich alkali-bearing aggregates, which can be identified in an alkali leaching test by immersion in alkaline solutions, can release up to 1.75 kg $Na_2O/m^3$ of concrete if used as fine fraction and up to 0.24 kg $Na_2O/m^3$ of concrete if used as coarse fraction. However, no clear $K^+$ contribution from aggregate was observed.

## 1. Introduction

Alkali-silica reaction (ASR) is a deleterious reaction affecting many concrete structures around the world, leading to excessive cracking, serviceability issues and reduction of the structure durability. This reaction, which involves unstable siliceous phases contained in fine and/or coarse aggregates, needs three essentials conditions to take place: (1), the aggregate is potentially reactive, (2), the concrete pore solution has a high alkali concentration, and (3), the concrete is exposed to high humidity conditions [1]. Generally, the higher the alkali concentration in the concrete pore solution, the greater the expansion due to ASR; in fact, $(OH)^-$ anions are released into the pore solution from portlandite ($Ca(OH)_2$) to establish equilibrium with $Na^+$ and $K^+$ cations. The high pH of the pore solution leads to the dissolution of metastable, amorphous, poorly crystalline or micro/crypto-crystalline forms of silica contained in some types of aggregates. The silica now in solution reacts with alkalis and calcium cations to form a gel, which imbibes water and increases in volume, leading to cracking of concrete [1].

Stanton [2], who identified the reaction in the late 30's, demonstrated that using low alkali cement can prevent ASR. However, some later studies showed that this preventive method has not been effective in reducing excessive expansion with some types of aggregates [3,4]. Although it was found that the alkali threshold above which deleterious ASR expansion occurs indeed varies from one aggregate to another, these observations also suggested that the cement was likely not the only source of alkalis to the pore solution to promote ASR in concrete.

### 1.1. Cement alkali contribution and effect of hydration on the composition of the pore solution

The most important source of alkalis to the pore solution of concrete is the portland cement. Indeed, alkalis occur in clinker in various phases. If sulfates are available in the kiln, alkalis tend to form potassium sulfate ($K_2SO_4$), sodium-potassium sulfate ($(K, Na)_2SO_4$) and calcium-potassium sulfate ($K_2Ca_2(SO_4)_3$). If the amount of sulfate is not sufficient to bind all alkalis, the remainders are distributed between the $C_3A$, $C_2S$ and, in a smaller proportion, in $C_3S$ and $C_4AF$ [5]. However, not all alkalis in the cement are readily soluble. McCoy and Eshenour [6] found that the amount of immediately water soluble sodium and potassium vary from 10 to 60% of the total cement alkali content and that even after one year, a considerable proportion of alkalis might not dissolve in the concrete pore solution. The amount of soluble alkalis from the cement strongly depends on the constituents of the clinker. Indeed, alkali sulfates are considered to be readily soluble, while alkalis incorporated in calcium silicate and aluminate clinker phases are considered poorly soluble and might only reach the pore solution when these phases hydrate [7]. On the other hand, when cement hydrates, some alkalis can be bound in the formation of C—S—H gel, depending on the Ca/Si ratio and the alumina content of the C—S—H. Indeed, a lower Ca/Si ratio fosters alkali binding [8,9]. Vollpracht et al. [10] made a review of a great number of experiments

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**Table 1**
Alkali release by aggregates stored in various extraction solutions (adapted/updated from Bérubé and Fournier, 2004).

| Authors | Material | Duration | Temperature (°C) | Sample shaking | Aggregate: solution ratio | Mass (g) | Material size | Extraction solution | Soluble alkalis (% $Na_2O_{eq}$) | kg $Na_2O_{eq}/m^3$ of concrete[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Van-Aardt and Visser (1977) | 6 Feldspars, 2 clay minerals | 250 days | 39 | No | 1:50 | 0.5 | Powder | 25 mL Saturated lime[b] | 0.01–2.32 | 0.37–44.03 |
| Stark and Bhatty (1986) | 3 Feldspars, 3 sands, 3 gravels, 1 andesite | 90 days | 38 | Yes | 1:5 | 5 | < 80 μm | 25 mL Saturated lime | 0.26–1.99 | 4.81–36.82 |
|  | 3 Feldspars, 1 andesite | 28 days | 80 | No | 1:5 | 5 | < 80 μm | 25 mL Saturated lime | 0.83–5.03 | 15.36–93.06 |
|  |  |  |  |  |  |  |  | 25 mL Distilled water | 0.03–0.13 | 0.56–2.41 |
| Kawamura et al. (1989) | 2 Andesites | 180 days | 40 | Yes | 1:2 | 100 | 0.15–5 mm | 200 mL Saturated lime | 0.02–0.07 | 0.37–1.30 |
| Bérubé and Duchesne (1996) | 17 Different aggregates | 578 days | 38 | Yes | 1:1 | 40 | 1.25–5 mm | 40 mL Distilled water | 0.001–0.151 | 0.02–2.79 |
|  |  |  |  |  |  |  |  | 40 mL Saturated lime[b] | 0.002–0.11 | 0.037–2.04 |
|  |  |  |  |  |  |  |  | 40 mL Alkaline solution[c] | > 0.004–0.684 | 0.07–12.65 |
| Le Roux et al. (1997) | 8 Different aggregates | 7 h | 100 | No | 1:1 | 500 | 0.08–20 mm | 500 mL Saturated lime[b] | 0.0085–0.21 | 0.16–3.89 |
| Ouali (1997) | 7 Different aggregates | 1000 h | 60 | No | 1:4,2 | 120 | 0.08–0.63 mm | 500 mL Alkaline solution[c] | 0.008–0.47 | 0.15–8.69 |
| Lu et al. (2006) | Gneiss, granite, K-feldspar | 28 days | 80 | Yes | 1:2 | 25 | 10–12 mm | 50 mL Saturated lime[b] | 0.006–0.016 | 0.11–0.296 |
|  |  |  |  |  |  |  | 5–10 mm | 50 mL Saturated lime[b] | 0.007–0.029 | 0.13–0.54 |
|  |  |  |  |  |  |  | 1.25–5 mm | 50 mL Saturated lime[b] | 0.011–0.037 | 0.20–0.68 |
|  |  |  |  |  |  |  | 0.63–1.25 mm | 50 mL Saturated lime[b] | 0.015–0.046 | 0.28–0.85 |
|  |  |  |  |  |  |  | 0.15–0.63 mm | 50 mL Saturated lime[b] | 0.022–0.064 | 0.41–1.18 |
|  |  |  |  |  |  |  | 0.08–0.15 mm | 50 mL Saturated lime[b] | 0.051–0.112 | 0.94–2.07 |
| Wang et al. (2008) | Nepheline, alaskite | 24 h | 150 | No | 1:1 | Unknown | 0.15–0.65 mm | Saturated lime | – | 0.093–0.118[d] |
|  |  |  |  |  |  |  |  | Alkaline solution[c] | – | 0.236–0.490[d] |
| Locati et al. (2010) | 2 K-Feldspars, 2 Na-feldspars | 24 h | 80 | No | 1:10? | 25 | 0.15–0.30 mm | Alkaline solution[e] | 0.009–0.016 | 0.17–0.30 |
| Berra et al. (2014) | 2 Aggregates | 180 days | 80 | No | 1:1 | Unknown | 0–4 mm | Alkaline solution[c] | 0.037–0.041 | 0.68–0.76 |
|  |  |  |  |  |  |  | 4–20 mm | Alkaline solution[c] | 0.011–0.015 | 0.20–0.28 |
| Soares et al. (2016) | 6 Granitic aggregates | 455 days | 38 | Yes | 1:4 | Unknown | 0–2 mm | Saturated lime | 0.024–0.045 | 0.45–0.83 |
|  |  |  |  |  |  |  | 4.75–9.5 mm | Saturated lime | 0.007–0.010 | 0.14–0.18 |
|  |  |  |  |  |  |  | 12.5–20 mm | Saturated lime | 0.005–0.007 | 0.09–0.13 |
|  |  |  |  |  |  |  | 0–2 mm | Alkaline solution[e] | 0.190–0.206 | 3.51–3.81 |
|  |  |  |  |  |  |  | 4.75–9.5 mm | Alkaline solution[e] | 0.131–0.153 | 2.43–2.84 |
|  |  |  |  |  |  |  | 12.5–20 mm | Alkaline solution[e] | 0.104–0.144 | 1.92–2.66 |
| Menéndez et al. (2016) | Granodiorite | 91 days | 60 | Unknown | 1:4 | Unknown | 0–4 mm | Alkaline solution[c] | – | 6.29 |

[a] For a concrete containing 1850 $kg/m^3$ of aggregates.

[b] Saturated lime solution with solid lime in excess.

[c] 0,7 M KOH to measure Na release and 0,7 M NaOH to measure K release.

[d] For a concrete containing 0,1 $m^3$ of interstitial solution of a 0,7 mol/L $Na_2O_{eq}$ concentration by $m^3$ of concrete.

[e] 1 M KOH to measure Na release and 1 M NaOH to measure K release, lime saturated.