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Lithium migration in a two-chamber set-up as treatment against expansion due to alkali–silica reaction

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HIGHLIGHTS

- A study on two-chamber lithium migration as treatment against ASR is presented.
- If not followed by cracking, ASR progress hinders migration due resistivity gain.
- The effects of different treatments on ASR expansion were evaluated.
- Lithium migration led to the lowest post-treatment ASR expansion levels.

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ABSTRACT

Alkali–silica reaction (ASR) affects numerous concrete structures worldwide. However, the intervention options for ASR in existing structures are limited. Lithium is proposed to suppress expansion. In this paper, an investigation on two-chamber lithium migration as treatment against ASR is presented. First, the influence of different levels of ASR development on lithium migration is studied. Results show that ASR development, if not followed by enough crack formation, hinders migration due to increase in resistivity. Second, the effects of different treatments, such as sodium and potassium removal, lithium migration (combined with the associated sodium and potassium removal) and lithium diffusion, on ASR expansion were evaluated. Lithium migration led to the lowest post-treatment expansion levels.

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1. Introduction

Numerous concrete structures worldwide are affected by alkali–silica reaction (ASR). Nevertheless, the currently available repair options are limited. The addition of lithium compounds into fresh concrete mixture has been acknowledged to prevent or reduce ASR expansion since the 1950s (e.g. [1–3]). It is generally agreed that the presence of lithium salts alters the reaction mechanism either by hindering the formation of the ASR gel or by modifying the gel into a less expansive product [4–7]. With regard to treatment of existing structures, the incorporation into the fresh mixture is, obviously, no longer possible. In this case, lithium needs to be transported into the material. Studies have shown that, when compared to other techniques such as immersion, vacuum impregnation and wet and dry cycles, electrochemical migration is the

most effective method to drive lithium ions into hardened concrete [8,9].

Several authors have investigated electrochemical lithium migration in concrete and mortars (e.g. [8–15]). However, there is still no consensus on the effectiveness of lithium migration as a treatment against deleterious ASR expansion. Indeed, deeper understanding of the basics behind lithium migration and its effects on ASR affected concrete is still necessary.

In this paper, an investigation on electrochemical lithium migration in a two-chamber set-up is presented. During electrochemical treatments, such as electrochemical chloride extraction, the reinforcement is often used as the cathode. In this type of configuration, sodium and potassium ions are attracted by the cathode and tend to accumulate in the region around it [16,17]. This accumulation increases the pH and may lead to further ASR development. In a two-chamber set-up, however, sodium and potassium ions are removed from pore solution of the specimen [18], which may further contribute to the prevention of future ASR expansion. In this work, the influence of different levels of expansion due to

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Table 1
Cement composition, wt% of cement.

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	P ₂ O ₅	K ₂ O	TiO ₂	Na ₂ O	Other	L.O.I. ^a
65.00	18.33	4.42	3.38	3.01	2.02	0.57	0.46	0.37	0.28	0.53	1.60

^a L.O.I.: loss on ignition.

ASR development on lithium migration is discussed. Finally, the effects of treatments such as lithium migration, sodium and potassium removal and lithium diffusion, on ASR expansion are presented.

2. Experimental program

2.1. Materials and specimen preparation

Concrete specimens were prepared with water to cement ratio (w/c) of 0.4 and Ordinary Portland cement type CEM I 42.5 N, commercially available in the Netherlands, with chemical composition shown in Table 1. The fine portion of the aggregate was non-reactive siliceous sand. The coarse aggregate was an Icelandic gravel, provided by Mannvit, which has shown to be ASR reactive elsewhere [19]. The gravel was analyzed by polarized light microscopy which revealed that the volcanic rock contained glassy groundmass. Volcanic glass is known to be ASR reactive in some cases [20,21].

NaOH was added to the mixture so that the Na₂O_{eq} (sodium oxide equivalent¹) by mass of cement was 1.25 wt%. The total Na₂O_{eq} of the concrete was 5.9 kg/m³. The proportions of the materials used are shown in Table 2. The mixing procedure was carried out following the recommendations on RILEM Recommended Test Method: AAR-4.1 [22], using a mixer. Firstly, the fine and coarse aggregate were mixed for one minute. Secondly, NaOH was mixed into half of the water. This solution was added to the aggregates and mixed for another minute. Finally, after a one-minute pause, cement and the rest of the water were added and the concrete was mixed for two minutes. Properties of the fresh mixture, namely slump and air content, are also shown in Table 2. The slump test was conducted according to [23]: the fresh mixture was compacted, in three layers, into a mold in the shape of a frustum of a cone (base diameter of 200 mm, top diameter of 100 mm and height of 300 mm). Then, the cone was withdrawn upwards the distance the mixture had slumped was measured. The air content was measured according to [24], by a pressure gauge meter. The mixture was placed in the container of the meter, compacted and leveled. The container was then closed and water was injected through one of the valves until it came out in the other valve. With the valves closed, air was pumped into the air chamber until the hand on the pressure gauge was on the initial pressure line. Finally, the main air valve was opened and air content was read in the pressure gauge.

The concrete (without any treatment) had its expansion behavior evaluated following the recommendations in [22] (the procedure will be described in the next subsection) and it can be classified as ASR reactive, with an expansion of 0.035 ± 0.004% by week 15.

Cylindrical specimens, with a diameter of 98 and 50 mm of height, were cast in order to evaluate the effects of ASR induced expansion on lithium migration. In order to evaluate the effects of lithium migration on expansion, concrete prisms (280 × 75 × 75 mm) were cast with stainless steel studs at the ends of each prism, positioned at the middle of the cross-section. After curing for a day, the specimens were demolded. The prismatic specimens were placed in stainless steel containers while

Table 2
Material proportions and properties of fresh concrete mixture.

Material	
Cement CEM I 42.5 N (kg/m ³)	488
Water, w/c = 0.4 (kg/m ³)	195
Fine aggregate <4 mm (kg/m ³) ^a	471
Coarse aggregate 4–16 mm (kg/m ³) ^b	1114
NaOH (kg/m ³)	4.0
Slump (mm)	180
Air content (%)	0.8

^a Non-reactive siliceous (river) sand.

^b Reactive Icelandic gravel (rounded and used as received).

the cylindrical ones were placed in plastic boxes. Both containers had a film of water on the bottom and metallic grids to avoid the direct contact of the specimens with the water. The containers were closed and placed in an ASR reactor, at 60 °C and R.H. of 100%. In order to avoid stray current corrosion of the studs during the migration experiments, as observed in a different series of tests [25], they were removed in week 5, the holes were filled with repair mortar and new external stainless steel studs were glued with a two-component adhesive.

2.2. Methods

The migration experiments were conducted in two-chamber migration cells. In this type of cell, a specimen is placed between two acrylic chambers filled with solutions, each with a titanium mesh as electrode. When an electric potential is applied between the electrodes, cations are attracted by the cathode (negative electrode), whereas anions move in the opposite direction, towards the anode (positive electrode).

The cylindrical specimens were tested in set-ups similar to the one described by ASTM-C1202 [26], as shown in Fig. 1. The anolyte was a 4.9 M LiOH solution while the catholyte was a saturated Ca(OH)₂ solution. LiOH 4.9 M solution was chosen because of its high lithium concentration and high pH, which prevents the acidification of the solution and deterioration of the concrete [18]. The applied voltage was 26.7 V (0.53 V/mm) and the test lasted four weeks. The specimens were submitted to migration after curing for 3 or 10 weeks in an ASR reactor (60 °C and R.H. of 100%). Two replicates per curing time were used.

In the case of the prismatic specimens, prismatic acrylic cells were used (Fig. 1). Two solutions were used as anolyte: a LiOH 4.9 M or a saturated Ca(OH)₂ solution. The use of Ca(OH)₂ was intended for the evaluation of the isolated effect of the removal of sodium and potassium ions on ASR induced expansion. Saturated Ca(OH)₂ solution was used as catholyte in all tests. The applied voltage was 40 V (0.53 V/mm) and the migration tests lasted four weeks. Although the applied voltage is different from the one applied in the experiments with the cylindrical specimens, the magnitude of the electric fields is the same in both cases. Therefore, the migration results should be comparable.

Besides migration tests, diffusion experiments (without current) were also conducted with the same solutions for four weeks. The diffusion experiments with Ca(OH)₂ in both chambers can be considered as the control case, as the specimens did not receive any treatment and were exposed to similar environmental condi-

¹ wt%Na₂O_{eq} = wt%Na₂O + 0.658 wt%K₂O.

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