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Modeling of early age loss of lithium ions from pore solution of cementitious systems treated with lithium nitrate

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A B S T R A C T

Addition of lithium nitrate admixture to the fresh concrete mixture helps to minimize potential problems related to alkali-silica reaction. For this admixture to function as an effective ASR control measure, it is imperative that the lithium ions remain in the pore solution. However, it was found that about 50% of the originally added lithium ions are removed from the pore solution during early stages of hydration.
This paper revealed that the magnitude of the Li^+ ion loss is highly dependent on the concentration of Li^+ ions in the pore solution and the hydration rate of the cementitious systems. Using these findings, an empirical model has been developed which can predict the loss of Li^+ ions from the pore solution during the hydration period. The proposed model can be used to investigate the effects of mixture parameters on the loss of Li^+ ions from the pore solution of cementitious system.

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1. Introduction

Alkali-silica reaction (ASR) is the chemical reaction that occurs between hydroxyl ions present in the pore solution of hydrated cement paste and certain reactive silica phases present in aggregates used in concrete. To date, most attempts to mitigate ASR in concrete structures have focused on preventing and/or reducing the amount of gel formed by modifying the chemical environment in which it forms and expands [1–5].

Since the first report of McCoy and Caldwell [6] on the beneficial effects of lithium ions (Li^+) on ASR expansion, the use of lithium based chemical admixtures for the purpose of ASR mitigation has been extensively studied for more than 60 years. Subsequent studies by numerous researchers resulted in several proposed mechanisms by which lithium ions (Li^+) allegedly control the ASR. These include: a) formation of physical barrier composed of insoluble Si–Li reaction products [7–9], b) formation of less expansive Si–Li reaction products [1,10–13], c) decreased rate of repolymerization of ASR gel [14] and d) increased chemical stability of reactive silica exposed to pore solution [7,13, 15–17]. However, none of these mechanisms fully explains the role of lithium in controlling the ASR.

Among different lithium compounds which can be potentially used as admixtures to mitigate the ASR, lithium nitrate ($LiNO_3$) is considered to be the most effective. A primary advantage of $LiNO_3$ over the other lithium compounds is that it does not increase the concentration of OH^- ions, which results in eliminating the pessimum effect of other lithium compounds [18,19]. Bérubé et al. [20] also reported slight

decrease of pH value when $LiNO_3$ was added as an admixture into cement paste. In addition, $LiNO_3$ is compatible with other chemical admixtures [21] and does not significantly affect such properties of concrete as strength, electrical resistance, drying shrinkage, and resistance to freezing and thawing [22,23].

One of the problem associated with the use of lithium containing admixtures is that the significant amount of Li^+ ions initially added into the mix water is removed from the pore solution during early hydration period by being incorporated into the early-age hydration products [10,19,20,24]. Therefore, the actual amount of Li^+ ions available to control the ASR is greatly reduced.

The present paper provides the description of the process used to develop the model to predict the extent of Li^+ ion loss from the pore solution due to the cement hydration. The developed model is then verified using the independent dataset obtained from other sources [19,20,25]. The proposed model can estimate the amount of the Li^+ ions actually left in pore solution and is thus expected to provide a useful method to quantify the amount of Li^+ ions available in pore solution to control the extent of ASR.

2. Incorporation of Li^+ ions in the hydration products

As previously mentioned, the unfavorable property of Li^+ ions released into the pore solution is that they tend to be incorporated into the hydration products in much greater proportions than other alkalis such as sodium (Na^+) and potassium (K^+) ions [20]. In general, about half of originally added lithium is lost during early hydration, presumably absorbed by the hydrating cement. Diamond and Ong [10] reported that even in nonreactive aggregate mortars a significant amount of lithium (more than 40%) were removed from the pore solution after

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only 1 day. Collins et al. [13] also confirmed that lithium is more preferentially incorporated into at least one of the hydration products than other alkalis. As a result, lithium ions removed from the pore solution are (presumably) not available for suppression of ASR [19].

The phenomenon of this substantial loss of Li$^+$ ions during early stages of hydration has been recently studied quantitatively by Kim and Olek [24]. Based on the results of these studies, two important finding were reported: a) the loss of Li$^+$ ions from pore solution during the hydration is mainly the result of their incorporation in the developing (growing) hydration products and not the result of sorption by existing hydrates, and b) at any given age, an identical fraction of the Li$^+$ ions would be removed from the pore solution extracted from the mixtures prepared at the same water-to-cement ratio (w/c), regardless of the initial amount of the admixture used (see Fig. 1).

Previous studies on the loss of Li$^+$ ions [16,19,20,24,25] during the early hydration period focused on determining the change in the Li$^+$ concentration in the pore solution obtained from pastes or mortars. As such, these data reflected the combined amount of Li$^+$ ions incorporated into each of different cement hydrates and did not provide specific information regarding different Li-binding affinities of various cement hydrates.

3. Development of the model for prediction of the change in concentration of Li$^+$ ions in pore solution

The development of the mathematical model for the loss of Li$^+$ ions described in this paper started with the formulation of differential equation for the rate of loss of Li$^+$ ions from the pore solution ($r(t)$, mol·kg^{-1}·h^{-1}) normalized per kilogram of cement. This differential equation was then solved analytically in terms of $r(t)$, using the previously reported empirical model for the degree of hydration [26]. The resulting rate model allows for the determination of the concentration of Li$^+$ ions in the pore solution of the cementitious systems.

Once developed, the model was calibrated using the set of data previously reported elsewhere [24,25]. The model was verified using several additional sets of independent data, including: a) data from the work of Bérubé et al. [20], b) data from the work of Diamond [19] and c) data from the work of Kim [25]. All experimental data (concentration of lithium ions, total alkali content, age of specimens, and curing temperature) used for the model development and verification were obtained from the literature [19,20,24,25] and summarized in Table A.1 of the Appendix. The properties of cements used to produce paste and mortar

samples that were utilized in the process of model development and verification are given in Table 1. In cases where the fineness of cement used to prepare samples was not reported (e.g. C3, C4, and C5 cements) that value was arbitrarily assumed to be 370 m^2·kg^{-1} since the conventionally ground cement has the fineness within a range from 320 to 400 m^2·kg^{-1} [27].

3.1. Basic concepts and assumptions used in model development

The experimental results from work by Kim and Olek [24] were examined thoroughly to establish the relationship between the initial concentration of Li$^+$ ions (i.e. the concentration of Li$^+$ ions in the original mix water) and the amount of Li$^+$ ions lost from the pore solution during any given length of curing time. As shown in Fig. 1, for each of the curing periods examined a strong linear correlation can be observed between the initial concentration of Li$^+$ ions in mix water and the change in that concentration in the non-reactive mortar mixtures prepared at the same w/c. This linear relationship strongly indicates that the higher concentration of Li$^+$ ions in the pore solution will result in the proportionally higher decrease in the concentration during the hydration. Therefore, when developing the model, the rate of loss of Li$^+$ ions at a certain time t, [$r(t)$] was assumed to be directly proportional to the concentration of Li$^+$ ions in the pore solution at the same time t.

As reported elsewhere [24], the loss of Li$^+$ ions from the pore solution was the result of their incorporation within the developing hydration products. Since the rate of growth of hydration products is expected to be proportional to the hydration rate [28,29], it is also reasonable to assume that the rate of loss of Li$^+$ ions will be also proportional to the hydration rate.

It should be noted that the rate of loss of Li$^+$ ions, [$r(t)$] can be regarded as the average overall rate for cement hydrates. In other words, although different cement hydrates may remove Li$^+$ ions from the pore solution at different rates, such values will be difficult to measure in a system with multiple phases reacting more-or-less simultaneously. In this context, the use of an average rate of loss of Li$^+$ ions is more practical for modeling purposes.

When developing the model, it was assumed that the amount of pore solution is equal to the amount of free water present in the pores of the hydrated cementitious system and that bulk composition of the pore solution reflects the average concentration of the ions of interest. In addition, it was also assumed that the effect of the dosage of LiNO$_3$ on the hydration rate in the paste or mortar systems is not significant
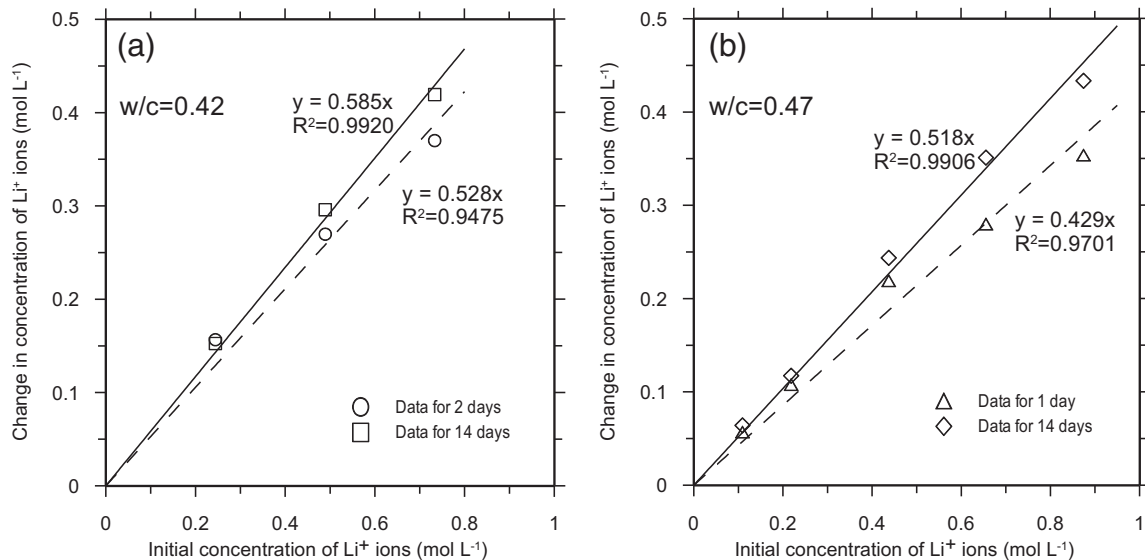

Fig. 1. Linear relation between the initial concentration of Li$^+$ ions and the change in concentration of Li$^+$ ions for mortar samples prepared with non-reactive aggregate: (a) mortar samples with w/c = 0.42 after 2 days and 14 days of curing; (b) mortar samples with w/c = 0.47 after 1 day and 14 days of curing. Data adopted from the reference [24].