



A mathematical model for the kinetics of the alkali–silica chemical reaction



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ABSTRACT

Starting from the chain of three chemical reactions which characterize the alkali–silica reaction (ASR), this paper attempts to develop a mathematical framework through which the reaction kinetics can be better understood. A petrographic support is given to better understand the physical implications of these equations, and to provide a reasonable support for the choice of the reaction rates.

First an analytical solution is sought. Though one was not found, three new conservation laws were derived. Then a numerical solution is applied, and important observations are made. First, and foremost, the role of water is confirmed, and then the outcome of the reaction when different concentrations of alkali and silica are used is derived. Finally, the temporal evolution of the expansive gel formation is contrasted with both macro-kinetics model, and diffusion based meta-model for the concrete expansions are compared.

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1. Introduction

The alkali–silica reaction (ASR) is a major factor contributing to concrete infrastructure aging (surpassed only by rebar corrosion induced by depassivation) and as such, is widely studied.

The chemistry of this reaction is complex [1] multi-staged [2] and is essentially an acid–base one. The acid reactant is silica in the solid state, the basic reactants are potassium and/or sodium hydroxide and possibly calcium in the pore solution. The reaction medium is water and the product of the reaction is a calcium potassium silicate hydrate, or a calcium sodium silicate hydrate [3], depending on the relative position to cement paste and the age of ASR gel that forms [4].

Alkalis are present in Portland cement in the form of alkali sulfates, alkali-aluminate, and in the solid solution of belite. Among these, alkali sulfates are the dominant and water-soluble phase, which means that the counter ion of the alkalis in the pore solution at the earliest stage of cement hydration is sulfate. Accordingly, when subsequent precipitation of ettringite is completed, the counter ion of the alkalis becomes hydroxide. This in turn will result in an increase of the pH of the pore solution while both alkali ions (Na^+ and K^+) and hydroxide ions (OH^-) will concentrate at a sufficiently high level to attack the reactive silica in the aggregate to form alkali–silica gel.

It should be noted that there is increasing evidence that alkalis can also be found in some aggregates (such as those extracted from rock containing feldspar, illite mica or volcanic glass). If the pH is above a

critical value, the alkali-containing silicates will release alkalis through the interaction with the alkaline pore solution in concrete and the reaction will be more severe than otherwise [5,6] In the following model, no distinction is made as to the source of the alkali.

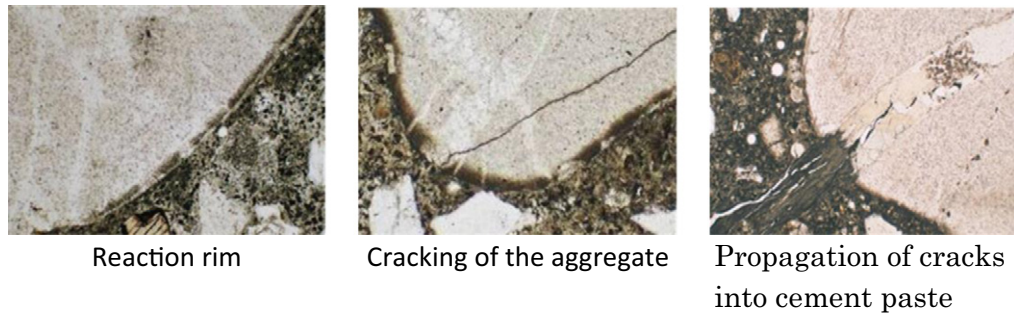
Silica, on the other hand, is the main constituent of most aggregates in the form of silicon dioxide (SiO_2). Reactive silica such as: 1) early-expansive (opal, cristobalite, tridymite, and chalcedony) and 2) late-expansive (cryptocrystalline and microcrystalline quartz) types, and 3) siliceous volcanic glasses (e.g. rhyolitic glass) are all present in siliceous rocks throughout the entire section of the aggregate [7] (Fig. 4d). From petrographic examinations, ASR proceeds in the following stages [4]: (i) formation of reaction rim, exudation (ii) rimming/exudation of sol/gel on the reacted aggregate partially filling microporosity in cement paste, (iii) cracking within reacted aggregate accompanied by gel-filling, (iv) propagation of radial gel-filled expansion cracks from the reacted aggregate into surrounding cement paste, and (v) precipitation of ASR gel into air voids along cracks distant from the reacted aggregate. Reaction rim is filled with interstitial ASR gel or its crystalline products (rosettes) showing a dark appearance in the transmitted light (Fig. 1(a)). Reaction rim develops conspicuously with the early-expansive aggregates (opaline shale, andesite, glassy rhyolite, etc.), whereas this rim is less marked on the late-expansive aggregates (schist, gneiss, quartzite, limestone, etc.), although it can be seen on the fracture surface. It should be noted that precipitation of ASR gel into air voids distant from the reacted aggregate is not the cause of expansion but a result of advanced ASR as a diagnostic feature in petrography.

From an evolutionary perspective, one can discern the following stages for the reaction: 1) nucleation, 2) development of the reaction,

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(a) Crack nucleation inside aggregate followed by propagation inside the cement paste [4]



(b) Proposed petrographic and evolutionary interpretation of ASR

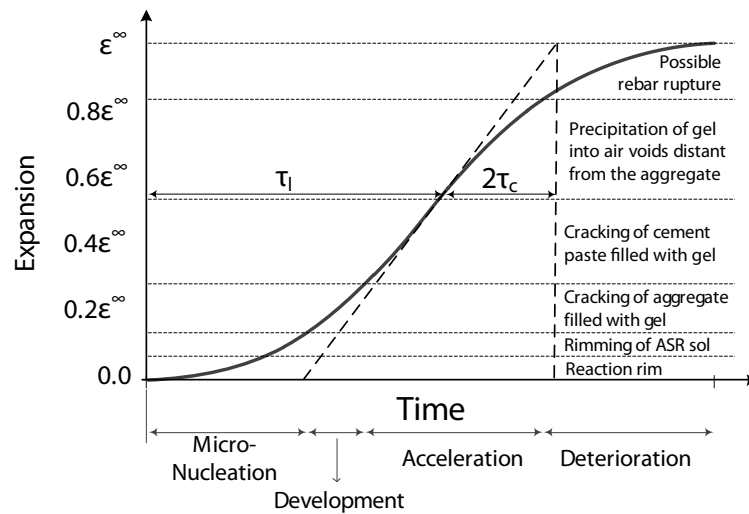


Fig. 1. Petrographic interpretation of the reaction.

3) acceleration of the reaction and deterioration, and finally 4) severe deterioration, Fig. 1(a). A proposed petrographic interpretation of the evolutionary trend of ASR is shown in Fig. 1(b).

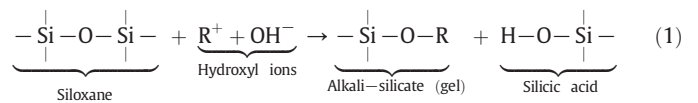
It should be noted that the reaction initiates from the periphery of the aggregate (stage 1) without producing expansion. Expansion starts inside the aggregate where alkali-rich ASR gel is confined within micro-textures of the reacted aggregate (stage 2). Concrete deterioration becomes more noticeable once the cement paste starts cracking, and deterioration proceeds by increasing the width and density of cracks (stage 3). Finally, severe damage occurs (stage 4) after active expansion of concrete, including structural failures (possible rupture of rebar, distortion, loss of structural integrity).

Larger aggregate tends to retain higher concentrations of OH and alkali ions inside the aggregate, hence formation of expansive alkali-rich ASR gel initiates inside coarse aggregate, rather than on the surface where calcium from the cement paste dominates. This explains the severe cracking typical in coarse aggregate, and the earlier termination of the reaction in fine aggregate.

Once ASR gel migrates from the reacted aggregate and reaches the cement paste, it takes up calcium and loses alkali thus its composition approaches the one of CSH gel and thus loses its potential for expansion, gradually leading to termination of the ASR [8]. This compositional change of ASR gel (the ratio of replacement of alkalis by calcium), which fills cracks from the reacted aggregate into cement paste, has also a “sigmoidal curve” suggestive of a diffusion process ([9] Fig. 5(a)).

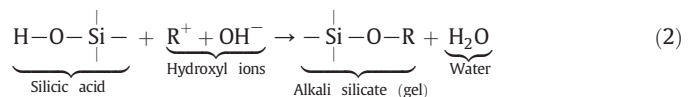
Whereas the majority of silicon dioxide is stable, the poorly crystallized silica are prone to react with the cement hydroxyl ions. For the

sake of simplification, many researchers assume the reaction to occur on the surface of the aggregate and to produce silanols (Si-OH groups). Initially, each atom of silicon is connected to the lattice by four siloxane bonds and will be ruptured by OH⁻ ions. Hence, in the first stage there is a hydrolysis of the reactive silica (siloxane) by OH⁻ ions to form an alkali-silica gel. In this hydrolysis reaction the high pH pore fluid reacts with Si-O-Si bonds to form silicic acid (silanol bonds) and alkali silicate gel. A characteristic of this equation is that the dense and relatively (compared to the cement paste) impermeable aggregates react very slowly



where R⁺ denotes an alkali ion such as Na⁺ or K⁺.

The silicic acid is weak, so that it immediately reacts with further hydroxyl liberating water and negatively charged Si-O-, thus readily abundant and mobile sodium, potassium and calcium ions will diffuse in the gel to balance the negatively charged species.



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