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

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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 (SiO₂). 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 soluble 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 (schist, gneiss, quartzite, limestone, etc.), whereas this rim is less marked on the late-expansive aggregates (sandstone, slate, andesite, glassy rhyolite, 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,
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 that 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 crystal-
lized 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
impervious aggregates react very slowly.

\[
\text{Siloxane} + R^+ + OH^- \rightarrow \text{Alkali–silicate gel (gel)} + \text{Silicic acid}
\]

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.

\[
\text{Silicic acid} + R^+ + OH^- \rightarrow \text{Alkali silicate (gel)} + \text{Water}
\]
The resultant alkali silicate (alkali silicate gel) is hygroscopic (expands in the presence of water).

\[
\begin{align*}
\text{Alkali–silicate (gel)} & \rightarrow \text{Expanded alkali silicate (gel)}
\end{align*}
\]

Eqs. (1)–(3) constitute one of many simplified models for the ASR and follow the notation of Ichikawa and Miura [2] though the first two can be traced back to the work of Powers and Steinour [10].

Finally, it should be noted that one could add a fourth equation to describe the termination of ASR in terms of the (very slow) ionic exchange by mutual diffusion between alkalis in ASR gel and calcium in cement paste, which results in the conversion of expansive alkali-rich ASR gel into non-expansive calcium silicate gel (CSH gel). This process can be enhanced by the percolation of Ca-bearing interstitial water into pre-existing ASR gel, which occurs during repeated drying and wetting, and freeze/thaw.

\[
\begin{align*}
-\text{Si}^- - & (\text{H}_2\text{O})_n + R^+ & + \frac{1}{2} \text{Ca}^{2+} & \rightarrow -\text{Si}^- - (\text{H}_2\text{O})_n + \text{Ca}^{2+} \\
\text{Expanded alkali silicate (gel)} & \text{Calcium substitution} & \text{Calcium silicate gel (CSH gel)} \nonumber
\end{align*}
\]

In the present study, this last equation will be ignored.

2. Problem formulation

Eqs. (1)–(3), which are second-order equations [11], are first rewritten as

\[
\begin{align*}
\text{Si}^- - & (\text{H}_2\text{O})_n + R^+ & + \frac{1}{2} \text{Ca}^{2+} & \rightarrow -\text{Si}^- - (\text{H}_2\text{O})_n + \text{Ca}^{2+} \\
\text{Expanded alkali silicate (gel)} & \text{Calcium substitution} & \text{Calcium silicate gel (CSH gel)} \nonumber
\end{align*}
\]

where \(k_i\) is the reaction rate. The objective of this study is to derive a single kinetic term which can characterize the reaction:

\[
k_{\text{ASR}} = f(k_1, k_2, k_3). \tag{8}
\]

First, the rate of change of concentration for each of the six constituents is written as [11]

\[
\frac{dA}{dt} = -k_A(A(t)B(t)), \tag{9}
\]

\[
\frac{dB}{dt} = -k_A(A(t)B(t)) - k_D(D(t)B(t)), \tag{10}
\]

\[
\frac{dC}{dt} = k_A(A(t)B(t)) + k_D(D(t)B(t)) - k_D(C(t)E(t)), \tag{11}
\]

\[
\frac{dD}{dt} = k_A(A(t)B(t)) - k_D(D(t)B(t)), \tag{12}
\]

\[
\frac{dE}{dt} = k_D(D(t)B(t)) - k_C(C(t)E(t)). \tag{13}
\]

\[
\frac{dF}{dt} = k_S(C(t)E(t)), \tag{14}
\]

where \(k_i\) is a positive real constant for \(i = 1, 2, 3\) and \(X\) is the concentration of substance \(X\) \((\text{mol} / \text{L})\) in moles per volume of solution.1 A solution is sought to this system of six coupled ordinary differential equations, with particular interest in the temporal evolution of \(F\) (the expanded gel).

Conceptually, the reaction rate \(k_S\) which governs the formation of gel should be related to the macro-kineti equation (Eq. 16), and to the diffusivities in Eqs. (17) and (18) in the meso-model. Those could only be linked by a multi-scale/physico-chemical “grand unifying model” which is precisely one of the greatest challenges confronting our research community. As a very small step toward such a solution, attempt is hereby made to simply determine \(k_S\).

Given the complexity of the problem, and the absence of directly related previous studies, the following effects are neglected: 1) Presence of calcium and alkali–calcium substitution [12]; 2) temperature; and 3) structural confinement [13], and 4) stoichiometry of the chemical reactions. Finally, it should be emphasized that to the best of the author’s knowledge (and through contacts with various researchers) the values of \(k_i\) have not been determined. Finally, the stoichiometry of the equations will not be accounted for.

3. Analogies with other models

3.1. With macro-scale kinetics

As all chemical reactions, ASR is a function of both time and temperature however, contrarily to most, time scale is measured in years. Hence, once the reaction has been detected (typically many years after construction), a critical question is how long before the reaction (and hence the expansion) stops. In other words, can we quantify the kinetics of the reaction? Indeed, the kinetics of the ASR has, surprisingly, received very little attention. One noteworthy exception is the work of Giorla [14] who highlighted the importance of the kinetics in terms of the microstructure.

Kinetics of ASR has been directly or indirectly explored by researchers according to the model adopted. At the macro-level (finite element of a structure) empirical (based on bar expansion) kinetics models have been developed. One of the earliest model was proposed by Capra and Bourmazel [15]

\[
\varepsilon(t, \theta) = \frac{1}{A_0} \left(1 - A_0 - e^{-k_A e^{-\frac{\tau}{T}}} \right) \varepsilon^\infty \tag{15}
\]

where \(\varepsilon^\infty\) is the maximum expansion, and \(A_0\) is a constant to be experimentally determined. More recently, many studies have adopted the kinetic model of Larive [16]

\[
\varepsilon(t, \theta) = \xi(t)\varepsilon^\infty = \frac{1 - e^{-\frac{\pi \theta}{4\tau}}}{1 + e^{-\frac{\pi \theta}{4\tau}}} \varepsilon^\infty \tag{16}
\]

where \(\theta\) is the absolute temperature, \(\pi \tau\) and \(\tau\) are the latency and characteristic times respectively, Fig. 2.

Analogous equations have been used by Comi et al. [17] in their analysis of major concrete structures. It should be noted that in these cases, the kinetic equations are empirical and applicable at a macro-scale study [18] such as the finite element analysis of a dam.

1 For convenience, the brackets customarily used to refer to the concentration \([X]\) were omitted.
3.2. With a meso-model

At the meso-level a single aggregate is (typically) modeled along with the cement paste. Transport equation is used to model gel, whose formation is first accommodated by its saturation of the capillary pores, [19,20,21,22]. Most of these models are based on the early-expansive ASR (andesite, glass) which develops reaction rim, while other models are based on the late-expansive ASR without a marked reaction rim [23,24] reflecting the geology of the local aggregate. In this context, kinetics (though this term is seldom used in these studies) is directly related to the diffusivity coefficients adopted. At this meso-level the penetration of alkali ions from the pore solution into the aggregate is numerically modeled.

A representative work is the one of Charpin and Ehrlacher [25] who assumed that the formation of the reaction rim leads to delamination of the aggregates. Puatatsananon and Saouma [26] considered a two phase diffusivity process and assumed the reaction to initiate at the periphery of the aggregate:

3.2.1. Penetration of alkali ions into the aggregate

Penetration of alkali ions into the aggregate assumed to be governed by Fick's law:

$$B_{\text{ion}} \frac{\partial C_{\text{ion}}}{\partial t} = \nabla (D_{\text{ion}} C_{\text{ion}}) \nabla C_{\text{ion}}$$

where $C_{\text{ion}}$ is the free ion concentration of the pore solution inside the aggregate, and $B_{\text{ion}}$ and $D_{\text{ion}}$ are the binding capacity and ion permeability of the aggregate, respectively. ASR occurs only when $C_{\text{ion}}$ reaches a critical concentration $C_{\text{cr}}$. It should be noted that this is a slow and continuous process, and the moving front (where $C_{\text{ion}} = C_{\text{cr}}$) varies with time $t$ as shown in Fig. 3(a). Because this is a rim-forming reaction, diffusion of alkalis occurs within the reaction rim, even its thickness is small, following the Fick's law.

3.2.2. Penetration of gel into the pores

The ASR gel permeation through the porous cement paste was assumed to be characterized by Darcy's law for a viscous flow as

$$\frac{\partial C_{\text{gel}}(t)}{\partial t} = \nabla \left( \frac{K_{\text{gel}}}{\eta_{\text{gel}}} \nabla P_{\text{gel}}(t) \right)$$

where $C_{\text{gel}}(t)$ is the concentration of the gel at time $t$, $K_{\text{gel}}$ is the permeability of the gel, and $\eta_{\text{gel}}$ is the viscosity of the gel. The reaction is assumed to occur within the reaction rim, even if its thickness is small, following the Fick's law.
where $C_{gel}$ and $\eta_{gel}$ are the concentration and viscosity of the gel, respectively. $K_{gel}$ is the gel permeability of the porous cement paste; $P_{gel}$ is the interface pressure distribution due to ASR gel (thus depends on the degree of saturation of the pores).

One must note the analogy between those two transport mechanisms with Eqs. (1) and (3) respectively. In their study, Puatatsanon and Saouma [26] have shown that a multi-scale analysis of ASR (starting with ion diffusivity) can lead to a macroscopic kinetic curve, Fig. 4.

This figure shows the superposition of the curve fitted model of Larive (Eq. [16]) to match the expansion kinetic obtained from a diffusion based simulation using aggregate size of 2.36 mm. It should be noted that a small time lag exists between the Larive’s sigmoidal model curve and the simulated curve, i.e. with the simulated model here the coarser fraction No. 8 of the aggregate starts slightly later than the sigmoidal model. This means that the coarser aggregate develops a reaction rim or a reaction zone saturated with expansive ASR gel, and that it can start to expand before saturation of ASR sol/gel (rimming/exudation of ASR sol around the aggregate) in the surrounding cement paste takes place, although they are broadly similar as a first approximation.

Finally, the kinetics of the ASR can be investigated through the prism of the chemical reaction itself where complete abstraction is made of the representative volume, and one focuses only on the reaction (such as Eqs. (1)–(3)). To the best of the authors knowledge, such a study has not been reported in the literature, and is precisely the theme of this paper. Present paper generalizes the kinetics of a wide range of ASR covering all the processes from decomposition of reactive silica, formation of ASR gel, to the swelling of ASR gel. As a first approximation, starting from the setup resembling the classical surface reaction mechanism, equations to predict the expansion force of the aggregate against cement paste were derived as a function of time, irrespective of whether expansive gel is formed at the interior of the aggregate, or within the reaction rim, or at the paste–aggregate interface. As a result, both the early-expansive ASR and the late-expansive ASR, which had been separately treated by previous researchers, are handled consistently by changing the parameters, and a Grand-Unifying model was proposed here.

4. Analytic solution

By mere observation of Eqs. (9)–(14) it can be noted that

$$\frac{d}{dt}[2A(t)−B(t)+D(t)]=0,$$

$$\frac{d}{dt}[A(t)+C(t)−E(t)]=0,$$

$$\frac{d}{dt}[B(t)+C(t)+F(t)]=0].$$

It thus follows that the functions inside the brackets are conserved quantities, constant for all time. As a result, new constants $M_1, M_2,$ and $M_3$ are introduced, satisfying

$$M_1 = 2A(t)−B(t)+D(t),$$

$$M_2 = A(t)+C(t)−E(t),$$

$$M_3 = B(t)+C(t)+F(t).$$

Hence, the ordinary differential equations for $A, B,$ and $D$ (in Eqs. (9), (10), and (12)) can be decoupled from the remaining three ones. Then Eq. (22) leads to

$$D = M_1 − 2A + B$$

and now Eqs. (9)–(10) are replaced by a second order system

$$\frac{dA}{dt} = −k_1AB,$$

$$\frac{dB}{dt} = −k_1AB−k_2B(M_1−2A+B).$$

This system will depend on the two rate constants $k_1$ and $k_2$, and is independent of $k_3$.

Solution hinges on first solving for $A$ and $B$, and then by substitution $D$. Then Eq. (11) is reintroduced in order to determine $C$ where the conservation law in Eq. (23) is used to replace $E$

$$\frac{dC}{dt} = k_1AB+k_2DB−k_3C(A+C−M_2).$$

Note that $D$ can be eliminated from the equation above using Eq. (22) if desired.

Once $A, B, C$, and $D$ are known, $E$ and $F$ can be determined from Eqs. (23)–(24). As a result, solving the sixth order system in Eqs. (9)–(14) amounts to solving a second order coupled system, Eqs. (25)–(26), and a single first order equation, Eq. (27). The three conservation laws Eqs. (22)–(24) determine the remaining three functions.

It is possible to reduce Eqs. (25)–(26) to a single second order differential equation in terms of $A$ or $B$ alone. This will yield

$$A'' = \frac{A'}{A} \left[ \left( 1 + \frac{k_2}{k_1} \right) A' + (2k_2−k_1)A^2−M_1k_2A \right].$$

or

$$B'' = \frac{1}{B} \left[ (B')^2−(k_1+k_2)B^2−k_1k_2B^2(B−M_1) \right].$$

where the primes denote derivatives with respect to time. Alternatively, one can use the conservation laws Eqs. (22)–(24) to write the evolution equation for $F$ as

$$F' = k_3(M_3−B−F)(M_3−M_2+A−B−F)$$

and $B$ can be expressed in terms of $A$ using Eq. (9)

$$B = −\frac{A'}{k_1A}.$$
Substituting into Eq. (30) yields an equation to solve for $F$ the expanded alkali silicate (gel):

$$F' = k_2 \left[ \frac{A}{k_1 A} - F \right] \left( M_3 - M_2 + A + \frac{A}{k_1 A} - F \right) = k_2 \left[ \frac{(M_3 - F)k_1 A + A}{(A - M_2)k_1} + (M_3 - F)k_1 A + A \right].$$ (31)

Unfortunately, attempts to solve Eqs. (28), (29), and (31) analytically failed. As a result, numerical solutions of Eqs. (9)–(14) will be investigated instead. Nevertheless, the quest for an analytical solution revealed some interesting results: the three conservation laws of Eqs. (22)–(24)

$$2\text{Siloxane} - [\text{Hydroxyl ions} + [\text{Silicic acid}] = \text{Cst.} \quad (32)$$

$$[\text{Siloxane}] + [\text{Alkali-Silicate}] - [\text{Water (generated)] = \text{Cst.} \quad (33)$$

$$[\text{Hydroxyl ions}] + [\text{Alkali-Silicate}] + [\text{Expanded alkali silicate}] = \text{Cst.} \quad (34)$$

5. Numerical solution

The numerical solution of the original first order equations Eqs. (9)–(14) is sought next. More specifically, the behavior of $A$, $B$, and $D$ will be examined first since the evolution equations for these functions can be decoupled from the equations for $C$, $E$, and $F$. Then temporal evolution of $C$ and $D$ will be addressed, and finally the most important product $F$ (expanded gel) will be addressed separately. The last three concentrations will be determined from the first three and the derived conservation laws.

5.1. Assumptions

Since molar concentration must be nonnegative, $A$, $B$, $C$, $D$, $E$, and $F$ are considered nonnegative, whereas $A(t = 0)$ and $B(t = 0)$ must be nonzero for an alkali–silica reaction to occur. It should be noted that $E(t = 0)$, will include both the water generated (Eq. (6)) and the initial presence of water $E_0 \geq 0$. For the sake of simplicity, it is further assumed that $C(t = 0) = D(t = 0) = F(t = 0) = 0$. While it is commonly assumed that the ASR is governed by the finite silica (i.e. $B(t = 0) \geq A(t = 0)$), the case where $A(t = 0) \geq B(t = 0)$ will also be considered.

A critical aspect of this study is the proper selection of the reaction rates $k_1$. Those are certainly not published in the literature, and indeed many researchers consulted indicated that they are unknown. However, a detailed analysis of these three reactions is hereby proposed:

Reaction 1: (Eq. (5)) depends on the potential reactivity of the type of mineral (for a given alkaliinity) through its internal specific surface area. For early-expansive ASR such as opal this reaction may take only 0.1 to 2 years, for cristobalite and tridymite 2–5 years. For moderately expansive ASR such as chalcedony and volcanic glass (rhyolitic) 5–10 years; finally for late-expansive ASR such as cryptocrystalline quartz 10–20 years and for microcrystalline quartz 20–30 years.

Reaction 2: (Eq. (6)) depends on the alkalinity of pore solutions available within aggregate, primarily controlled by the content of soluble alkalis in the cement used, and secondarily by the porosity and texture of the aggregate which has an influence on the accessibility of alkalis and OH ions, as well as on the efficiency of subsequent accumulation of alkali-rich ASR gel within aggregate to generate expansion. By definition, this may be a fast neutralization reaction, however this is not yet fully ascertained. However, unlike the diffusion of Ca into ASR gel at a later stage of ASR, both Na and OH at early stage of ASR may migrate via pore solution along the channel within reacted aggregate. Permeation of water into coarse aggregate can take a few seconds (porous rocks) or a few hours (very tight rocks). However, subsequent reaction to form ASR gel by neutralization will take longer due to the diffusion process within poorly organized reaction products. This could take anywhere between a few weeks, to at most 0.5 to 1 year. Reaction time may be shorter (order of a few hours to months) depending on the reactivity of the minerals previously mentioned for reaction 1 (highly reactive opal gathers alkalis very quickly at a pessimum proportion, but less expansive cryptocrystalline quartz does it very slowly). Contributions from long term alkali-release (order of decades) from alkali-bearing minerals in some rock types of aggregate are not counted here.

Reaction 3: (Eq. (7)) depends on the internal humidity of concrete. The reaction is nearly instantaneous: 10 s to minutes (when a dried ASR gel comes in contact with water along open cracks within a reacted aggregate at the concrete surface), or hours to weeks (when ASR gel is exposed to a different relative humidity near surface of a thin concrete member), or finally very slow: 0.5–1 years or more (large concrete section of a mass concrete). In the field, this reaction can be highly dependent on seasonal humidity variation (drying and wetting). This explains why laboratory tests at constant humidity tend to react faster than in the field.

During aging, expansion will continue until expansive alkali-rich ASR gel turns into a non-expansive calcium-rich silicate gel that resembles CSH gel (Eq. (4)), or into a non-expansive crystalline product (rosette), or simply after reactive mineral was totally consumed (e.g. opal). Formation, swelling and degradation of ASR gel do not occur simultaneously even within each aggregate particle in the same concrete. However, they overlap for a considerable span of time.

It is thus evident that there is no simple way to deterministically assign reaction rates to these equations, yet reasonable assumptions for the normalized values could be made. Henceforth, based on the above observations, one can reasonably assume that reactions 1, 2 and 3 (Eqs. (5), (6), (7)) take place over periods of 30, 1 and 0 years respectively, then normalizing with respect to $k_1 = 1$, we deduce that $k_2 = 50$, and $k_3 = 60$. For the sake of the numerical simulation these rates will be assigned values of $k_1 = 1$, $k_2 = 50$, and $k_3 = 100$.

Furthermore, and as stated earlier, the effect of temperature, confinement and type of aggregate, though critical, are hereby ignored for the sake of simplification.

Solution to the temporal ordinary differential equations was based on the Runge–Kutta algorithm for non-stiff equations [27] in MATLAB [28] (using the ODE45 function).

5.2. Asymptotic results ($t \to \infty$)

Asymptotic results as $t \to \infty$ are summarized in Table 1 (where $X_0$ denotes the initial condition $X(t = 0)$ for $X = A, B, C, D, E,$ and $F$) and details explained below.

We observe that (as expected) 1) $A$ and $B$ are always decreasing (with $B$ generally decreasing at a faster rate than $A$); 2) $F$ is always increasing; 3) $A, B,$ and $D$ are not affected by $E$; and 4) the initial condition $E(t = 0)$ only affects $C, E,$ and $F$.

5.3. Evolutions of $A(t)$, $B(t)$, and $D(t)$

Again, note that the initial conditions are $C_0 = D_0 = F_0 = 0$, while $A_0$ and $B_0$ are positive. $E_0$ can be positive or zero. Additionally, recall that
the conserved quantities in Eqs. (22)–(24) can be determined using the initial data. In particular, the conserved quantities can be given in terms of the initial data as

\[ 2A_0 - B_0 = M_1, \quad (35) \]
\[ A_0 - E_0 = M_2, \quad (36) \]
\[ B_0 = M_3. \quad (37) \]

It follows from Eqs. (9), (10), and (12) that at \( t = 0 \), \( A' = B' = -D' = -kDB \). Once \( D \) has slightly increased away from zero, the \( -kDB \) term in Eqs. (10) and (12) quickly starts to dominate as \( k_1 \) is larger than \( k_1 \). As a result, \( B \) starts to decrease faster than \( A \). Simultaneously, \( D \) also starts to decrease, approaching zero faster than either \( A \) or \( B \).

When \( D \) is sufficiently close to zero, \( A \) and \( B \) have approximately the same rate of decrease. The initial conditions \( A_0 \) and \( B_0 \) determine the asymptotic behavior of \( A \) and \( B \) for large time.

At this juncture, two cases are considered:

**Case 1.** \( B_0 \geq 2A_0 \)

In this case it follows from Eq. (35) that \( M_1 \leq 0 \). Since \( D \) approaches zero asymptotically, Eq. (22) implies that \( B(t) \geq 2A(t) \) for large time. With \( A \) and \( B \) always decreasing, at least one of the functions must eventually approach zero, forcing the other function to approach a constant. Since \( B(t) \geq 2A(t) \) for sufficiently large \( t \), it follows that \( A \to 0 \) as \( t \to \infty \), while \( B \to -M_1 = B_0 - 2A_0 \). Fig. 5(a) and (b) illustrates those results for \( A_0 = 1, B_0 = 2.5, C_0 = D_0 = F_0 = 0 \). Notice that \( A \to 0 \) for large time while \( B \to B_0 - 2A_0 = 0.5 \). In Fig. 5(a) water is depleted (the generated mass being much lower than \( E_0 \)), while in Fig. 5(b) it is produced. As expected, the former results in a quantity of expanded gel about twice the second. This is explained further in Sections 5.4–5.5.

**Case 2.** \( B_0 < 2A_0 \)

It follows from Eq. (35) that \( M_1 > 0 \), thus for large time \( B(t) \leq 2A(t) \). Consequently, for large time, \( B \to 0 \) and \( 2A \to M_1 \). That is, \( A \to \frac{1}{2}M_1 = A_0 - \frac{1}{2}B_0 \). Fig. 6(a) and (b) illustrates those results for \( A_0 = 1, B_0 = 1.5, C_0 = D_0 = F_0 = 0 \). Notice that \( A \to A_0 - \frac{1}{2}B_0 = 0.25 \) and \( B \to 0 \).

Same observations can be made with respect to water and generation of expanded gel as in the previous case. Finally, in the case of limited alkali, and irrespective of the initial water content, less expanded gel is generated.

5.4. Evolutions of \( C(t) \) and \( D(t) \)

Next, we return to the evolution equation for \( C \) using Eq. (11) or (27), \( C \) increases quickly for short time, until \( D \) (and eventually \( A \) or \( B \)) becomes sufficiently close to zero.

From Eq. (13), \( E = 0 \) initially. As with \( C \), once \( D \) becomes nonzero, if \( E_0 \) is small enough, then the behavior of \( E \) is dominated for a short time by the growth term \( kDBC \) in Eq. (13). However, after \( D \) decreases back to zero, \( E \) decreases again. If \( E_0 \) is relatively large, then the decay term \( -k_CE \) dominates (since \( k_1 > k_3 \)), so that \( E \) starts to decrease quickly. In either case, Table 1 summarizes how \( C \) and \( E \) will approach zero or a positive constant as \( t \to \infty \), depending on the relative values of \( A_0 \), \( B_0 \), and \( E_0 \). Again, two cases are considered.

**Case 1.** \( B_0 \geq 2A_0 \)

Recall that \( A \to 0 \) and \( B \to B_0 - 2A_0 \) as \( t \to \infty \). Two subcases are further considered.

- (a) \( E_0 \geq A_0 \): From Eq. (36), \( M_2 \leq 0 \). Since \( A \) approaches zero for large time, Eq. (23) implies that \( C \to E \to M_2 \) as \( t \to \infty \). It follows that \( C(t) \leq E(t) \) for large time. Moreover, because \( E \) is decreasing for large time, \( C \) must also decrease in order to remain smaller than \( E \) as \( t \to \infty \). In particular, \( C \) approaches zero, while \( E \to -M_2 = E_0 - A_0 \). These results are illustrated by Fig. 5(a), which depicts the solutions to Eqs. (9)–(14) when \( A_0 = 1, B_0 = 2.5 \), and \( E_0 = 2 \). Notice in the figure that \( C \to 0 \) as \( t \) increases, while \( E \to E_0 - A_0 = 1 \).

- (b) \( E_0 < A_0 \): From Eq. (36), \( M_2 \geq 0 \). As a result, Eq. (23) indicates that for sufficiently large time, \( C(t) \geq E(t) \), \( C \) continues to decrease until it approaches zero. Hence, \( C \to M_2 = A_0 - E_0 \) as \( t \to \infty \). Fig. 5(b) demonstrates a specific case in which \( A_0 = 1, B_0 = 2.5 \), and \( E_0 = 0 \). In particular, \( E \to 0 \) and \( C \to A_0 - E_0 = 1 \) for large time.

**Case 2.** \( B_0 < 2A_0 \)

In this case, \( A \to A_0 - \frac{1}{2}B_0 \) and \( B \to 0 \) as \( t \to \infty \). Consequently, for large time, Eqs. (23) and (36) yield \( A_0 - \frac{1}{2}B_0 + C(t) - E(t) \to M_2 = A_0 - E_0 \).

Simplifying,

\[ C - E \to \frac{1}{2}B_0 - E_0. \quad (38) \]

Again, two sub-cases are considered.

- (a) \( E_0 \geq \frac{1}{2}B_0 \): Eq. (38) leads to \( C(t) \leq E(t) \) for large time. As in the previous case, \( E \) is decreasing as time increases, thus for \( C \) to
stay smaller than $E$ as time increases, $C$ should also be decreasing. In particular, $C \to 0$ as $t \to \infty$, while $E \to E_0 - \frac{1}{2} B_0$ from Eq. (38). Fig. 6(a) shows the solutions to Eqs. (9)-(14) with $A_0 = 1, B_0 = 1.5$, and $E_0 = 2$. Notice that in the figure, $C \to 0$ and $E \to E_0 - \frac{1}{2} B_0 = 1.25$.

(b) $E_0 < \frac{1}{2} B_0$: In this case, Eq. (38) implies that $C(t) > E(t)$ as time increases. It follows that $E$ continues to decrease until it approaches zero, while $C$ approaches the constant $\frac{1}{2} B_0 - E_0$ as $t \to \infty$. This behavior is exhibited in Fig. 6(b), which depicts the solutions to the ODEs with $A_0 = 1, B_0 = 1.5$, and $E_0 = 0$. Notice that $E \to 0$ and $C \to \frac{1}{2} B_0 - E_0 = 0.75$ for large time.

Fig. 7 further depicts the results of Table 1 for the asymptotic behavior of $C$ and $E$ as $t \to \infty$ (using $A_0 = 1$ and $B_0 = D_0 = E_0 = 0$). It should be noted that the top right region of each graph corresponds to the first column of Table 1 (Case 1(a)), the bottom right region corresponds to the second column (Case 1(b)), the top left region of the graph corresponds to the third column of Table 1 (Case 2(a)), and the bottom left region corresponds to the fourth column (Case 2(b)).

Fig. 7(a) is a contour plot of $C(t = 10)$ as a function of the initial conditions $B_0$ and $E_0$, where $C(t = 10)$ represents the behavior of $C$ for long times. The following zones are identified:

**Case 1(a).** (upper right)

$B_0 \geq 2A_0$ and $E_0 \geq A_0$: $C(10) \approx 0$

**Case 2(a).** (upper left)

$B_0 < 2A_0$ and $E_0 \geq \frac{1}{2} B_0$: $C(10) \approx 0$

**Case 1(b).** (lower right)

$B_0 \geq 2A_0$ and $E_0 < A_0$: $C(10)$ is approximately independent of $B_0$. This is reasonable because $C(10) \approx A_0 - E_0$; since $E_0$ is on the $y$-axis, there are horizontal contour lines in this region. Furthermore, since $A_0 = 1$ was assumed, the value of $C(10)$ on each horizontal contour line is approximately $A_0 - E_0 = 1 - E_0$.

**Case 2(b).** (lower left)

$B_0 < 2A_0$ and $E_0 < \frac{1}{2} B_0$: the contour lines are linear with slope approximately $\frac{1}{2}$. This tells us that $C \to \frac{1}{2} B_0 - E_0$ as $t \to \infty$, thus it is reasonable that in Fig. 7(a), contour lines are of the form $E_0 \approx \frac{1}{2} B_0 - C(10)$.

Similarly, Fig. 7(b) depicts a contour plot of $E(t = 10)$ as a function of the initial conditions $B_0$ and $E_0$. Again, the behavior of $E(t)$ represents the behavior of $E$ for long times. The distinct behaviors of $E$ in the four regions of the plot can be clearly identified.

**Case 1(b).** (lower right)

$B_0 \geq 2A_0$ and $E_0 < A_0$: then $E(10) \approx 0$.

**Case 2(b).** (lower left)

$B_0 < 2A_0$ and $E_0 < \frac{1}{2} B_0$: then $E(10) \approx 0$.

**Case 1(a).** (upper right)

$B_0 \geq 2A_0$ and $E_0 > A_0$: $E(10)$ is approximately independent of the initial condition $B_0$. This is expected since $E \to E_0 - A_0$ in this case.

**Case 2(a).** (upper left)

$B_0 < 2A_0$ and $E_0 \geq \frac{1}{2} B_0$: $E(10)$ is approximately independent of the initial condition $B_0$. This is expected since $E \to E_0 - A_0$ in this case.
5.5. Evolution of $F(t)$

Finally, the behavior of the final product in the reactions, $F$ (expanded gel), is considered. From Eq. (14), $F$ is always increasing. Since $C_0 = 0$, $F = 0$ initially. Once $C$ starts to increase away from zero, $F$ starts to grow. However, at least one of the two quantities $C$ and $E$ will start to approach zero as time increases. Consequently, $F \to 0$ as $t \to \infty$, so that $F$ approaches a positive constant. The four possibilities for this constant are again summarized in Table 1. As with the other functions, this behavior is most easily explained using the previously derived conservation laws Eqs. (22)–(24) and Eqs. (35)–(37).

Case 1. $B_0 \geq 2A_0$

Recall that if $B_0 \geq 2A_0$, then $B \to B_0 - 2A_0$. From Eqs. (24) and (37),

$$B_0 - 2A_0 + C + F \to M_3 = B_0$$

after a sufficiently long time. That is

$$C + F \to 2A_0.$$  \hspace{1cm} (39)

Again, two sub-cases are considered:

(a) $E_0 \geq A_0$: In this case, $C \to 0$ as $t \to \infty$, so that $F \to 2A_0$. This behavior is illustrated in Fig. 5(a), where $B_0 = 2.5$, $A_0 = 1$, $E_0 = 2$, and $F \to 2A_0$. In other words, all the gel is hydrated.

(b) $E_0 < A_0$: Since $C \to A_0 - E_0$ in this case, it follows from Eq. (39) that

$$A_0 - E_0 + F \to 2A_0.$$

In other words, as $t \to \infty$, $F \to A_0 + E_0$. This behavior in turn is illustrated by Fig. 5(b), where $B_0 = 2.5$, $A_0 = 1$, $E_0 = 0$, and $F \to A_0 + E_0 = 1$ for large time. In this case less hydrated gel is generated.

Case 2. $B_0 < 2A_0$

Recall that $B \to 0$. From Eqs. (24) and (37)

$$C + F \to M_3 = B_0,$$  \hspace{1cm} (40)

Finally, the function $F(t)$ is shown in Fig. 8(a) for the cases considered in Figs. 5–6 with $k_1 = 1$, $k_2 = 50$, and $k_3 = 100$ and $A(0) = 1$, $C(0) = D(0) = F(0) = 0$.

It is worth noting that $F$ is larger when more water is present in the system and when the initial concentration of the alkali is larger. That is, $F$ takes on larger values when $E_0$ and $B_0$ are increased. This is precisely what is well known for ASR, that a minimum relative humidity of about 80% is needed for the reaction to be quantifiable [15].

Additionally, Fig. 8(b) depicts the same plot for small times, which shows that $F(t)$ has a slower growth rate for very small times. This initial growth rate is even slower for lower values of $k_1$.

The asymptotic behavior of $F$ is best illustrated by Fig. 9 which depicts a contour plot of $F(t = 10)$ as a function of the initial conditions $B_0$ and $E_0$. Indeed, $F(t = 10) \approx 2A_0 = 2$ throughout this region. This corresponds to the maximum amount of generated hydrated gel and agrees with the findings in Table 1.

Case 1a. (upper right)

$$B_0 \geq 2A_0$$ and $E_0 \geq A_0$: $F(10)$ is approximately constant, independent of both $B_0$ and $E_0$. Indeed, $F(t = 10) \approx 2A_0 = 2$ throughout this region. This corresponds to the maximum amount of generated hydrated gel and agrees with the findings in Table 1.

Case 1b. (lower right)

$$B_0 \geq 2A_0$$ and $E_0 \leq A_0$: contour lines are almost horizontal since $F(10)$ is approximately independent of $B_0$ here. This is reasonable because $F \to A_0 + E_0 = 1 + E_0$ as $t \to \infty$ in Case 1(b). In here the formation of hydrated gel is hampered by limited supply of water.

Case 2a. (upper left)

$$B_0 < 2A_0$$ and $E_0 \geq 1/2B_0$: the contour lines are approximately vertical, indicating that $F(10)$ is nearly independent of the initial condition $E_0$. Again, this is reasonable because in Case 2(a), $F \to B_0$ as $t \to \infty$, which
is evident in Fig. 9. In this zone formation of hydrated gel is hampered by limited supply of alkali.

Case 2b. (lower left)

\(B_0 < 2A_0 \) and \(E_0 = \frac{1}{2}B_0 \): the contours are approximately linear with negative slope. In Case 2(b), one expects that \(F(t) \approx \frac{1}{2}B_0 \) as time increases, so the contour lines in this region have the form \(E_0 \approx F(t) \approx \frac{1}{2}B_0 \). In this case limited supply of initial water and alkali caused reduced amount of generated hydrated gel.

Note that the numerical results depicted become more accurate, and agree better with the results in Table 1, if the equations are integrated for longer times. In Figs. 7 and 9, it was assumed that \(t = 10\) represented a sufficiently long time to observe the asymptotic behavior of the functions. One could increase this value of \(t\) to improve results.

6. Sensitivity analysis

It was noted at the beginning of Section 5.1 that the process of selecting values for \(k_1\), \(k_2\), and \(k_3\) is nontrivial. In spite of this difficulty, one can argue that as long as \(k_2\) and \(k_3\) are chosen to be sufficiently large relative to \(k_1\), then our results are not sensitive to changes in these rate constants.

Figs. 10 and 11 depict the long time behavior of \(F(t)\) as a function of \(k_2\) and \(k_3\) (holding \(k_1 \) constant at \(k_1 = 1\)) for each of the cases described in Table 1. It is clear that when \(k_2\) and \(k_3\) are both larger than \(10\), then the long time behavior of \(F(t)\) is constant and consistent with that described in Table 1. For instance, Fig. 10(a) depicts the behavior of \(F(t)\) for large time when \(A_0 = 1\), \(B_0 = 2.5\), and \(E_0 = 2\), which is an example of Case 1(a) \((B_0 \geq 2A_0 \) and \(E_0 \geq A_0\)). In this case, we expect that \(F(t)\) approaches \(2A_0\). Indeed, Fig. 10(a) shows that \(F \rightarrow 2A_0\) when \(k_2\) and \(k_3\) are both greater than 10. Similar results are observed in Fig. 10(b) for Case 1(b) and Fig. 11 for Case 2.

Since it is physically reasonable to assume that \(k_2\) and \(k_3\) are each at least ten times larger than \(k_1\), one can claim that the results of this paper, as summarized in Table 1, are relatively robust with respect to the choice of rate constants.

7. Comparison among models

Though the primary focus of this paper is the derivation of a mathematical model for the kinetics of the chemical reaction governing ASR, it is important to examine (albeit qualitatively) the results with the kinetics of other physical models.

Whereas Figs. 8(a) and (b) illustrate the evolution of the alkali-silicate gel, its trend compares well with the expansion of concrete as a result of ASR. As stated earlier, the generated gel, according to widely accepted classical models, originally based on the early-expansive ASR which develops a marked reaction rim would have first to fill up the pores within the aggregates before it can cause an expansion (in Fig. 3(b) it was assumed to fill up the cement paste first), corresponding to stage (ii) rimming/exudation of ASR sol. However, expansion of the aggregate may start whenever a reaction rim (early-expansive ASR) or an ambiguous reaction zone (late-expansive ASR) saturated with expansive ASR gel, stage (i), develops even before the cracking of the aggregate (stage (iii)) or the cracking of cement paste (stage (iv)) takes place.

Similarly, the trend compares well with the ASR expansion predicted by a multiscale model [26] where time is accounted for through the diffusivity coefficients of alkali ions into the aggregates (Eq. (17)) and of gel into the cement paste (Eq. (18)).

8. Conclusions

The preceding model is only a first attempt to improve our fundamental understanding of the kinetics of the chemical reaction governing ASR. It is hampered by a lack of data (kinetic rates), inconclusive basic understanding (the governing chemical reaction), and some simplifying assumptions (ignoring the effect of temperature and stoichiometry), yet some interesting results are obtained. More precisely:

1. Three nonintuitive conservation laws \((M_i, i = 1, 2, 3)\) are derived (Eqs. (32)–(34)).

2. Depending on the initial concentrations of the alkali and silica, estimates of the residual concentrations of these reactants at the end of the reaction are provided.
3. The importance of the initial concentration of water in gel formation is confirmed.

4. It is determined that the relative initial concentrations of the alkali, silica, and water in the system lead to four possible distinct estimates of the final concentration of the alkali silicate gel.

5. When alkali are in smaller supply than silica, a smaller amount of expanded gel is produced.

6. Qualitative similarities (sigmoidal curve) between the concentration of gel (chemical reaction) and the expansion of concrete under the ASR (physical macroscopic laboratory observations and diffusion based meso-models) are observed.

7. The parametric study indicates that results are relatively robust with respect to the choice of selected reaction rates.

In general, there are two major groups on the micromechanical model of ASR in concrete. They stemmed from the difference in the type of the reactive aggregates, i.e. the early-expansive ASR with pronounced reaction rims and the late-expansive ASR without reaction rims but with localized reactions inside the aggregate. Such a difference in the reactivity of the aggregates yielded various models for expansion. However, our study covers both the early- and the late-expansive ASR, which serves as a “Grand-Unifying” model. It is hoped that this small effort will stimulate further studies into the kinetics of the ASR, as it is absolutely critical to be able to ultimately predict the rate (and exhaustion) of the reaction. Finally, it would be highly desirable if a “Grand-Unifying” multi-scale/physico-chemical model be capable of reconciling meso-based diffusion models, macro-based observed bar expansions, and chemical based kinetics models. The first two models address the volumetric expansion, and the last model addresses the rate of gel formation. Such a model would be of great importance to assess the residual expansion of structures suffering from ASR.

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References


