An Application to the Diffusion Equation in a Model for the Damage in Concrete due to Alkali-Silica Reaction

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Abstract
This paper proposes a model for generation, diffusion and chemical damage due to the gel formed by alkali-silica reaction (ASR) in concrete. The first phase of the model takes into account the kinetics of chemical...
reactions, considering that the aggregate is reactive and alkali ions are available in solution porous concrete. The second stage is a diffusive model for RVE (Representative Volume Element) in the porous concrete area around the aggregate. The third stage uses the results of the first two phases to obtain a model for the chemical damage due to RAS. The created model is solved numerically, yielding a final result the chemical damage in a RVE of concrete.

**Keywords:** reaction alkali-silica, diffusion equation, chemical kinetics, damage model

1 Introduction

Since 1940 many researchers have devoted their research to the study of a concrete condition called alkali-aggregate reaction. This is a reaction that is likely to damage the concrete causing it to have a decreased resistance. Among the alkali-aggregate reactions, the best known and also most common is the alkali-silica reaction. This occurs when there reactive aggregate in the concrete together with the availability of alkali from the cement Portland and also a high degree of humidity. The humidity do the alkali and hydroxyl groups available for breaking the bonds of the siloxane and silanol type are present in the reactive aggregate. With the breakdown begins the formation of a gel which absorbs water and expands.

While there is capacity in the porous region next to the aggregate (transition region) to accommodate the gel, it will not crack. From the moment that this space becomes insufficient, the strain increases and starts cracking of concrete.

Many works have been made to create models which result in the expansion caused by alkali-silica reaction. The created models associate the expansion due to the following factors: moisture, concentration of alkali, aggregate reactivity and temperature. Some models include all factors and others just some of them. However, despite many created there is a complete model able to predict the expansion and the damage in terms of the aforementioned factors.

At work [1] Hobbs proposed a model based on a previous model [2] using an ordinary differential equation of first order. In this model, it is assumed that the amount of hydroxyl ions is sufficient for the reaction to occur. The theoretical model presented is based on the fact that the reaction rate is directly proportional to the amount of reactive aggregate. The model can predict the time to occurrence of cracks and also the expansion and predictions were in agreement with the observed behavior of mortar specimens containing opaline silica. This model is not limited to mortars and predicts the behavior of the expansion and cracking of the concrete, since it takes more energy to crack when compared to the concrete mortar.
In article [3] the authors developed a model for expanding mortar composed of silica glass particles on a Portland cement paste. The model assumes that a gel layer is created at the interface between the particles and the cement paste. The expansion of the mortar is given by the volume increase of the gel formed in the interface using the theory of elasticity. In the model, the intended expansion is slightly smaller than that observed.

The treaty model [4] is formed in two stages: the first is considered a diffusive process for hydroxyl and alkalis that come in contact with the aggregate yielding reaction and consequently the gel expands. In the second step is considered of the mortar due to expansion of the gel volume increase that exceeds the volume region around the porous aggregate can accommodate.

At work [5] the author created a mathematical model that combines the action of moisture, temperature, chemical and mechanical aspects of the RAS. The model is based on the mechanics of reactive multiphase materials in porous media with the theory of isotropic damage. The mass continuity equations, energy and momentum balance and constitutive and physical relationships required for modeling of the ASR in the variables humidity and temperature were developed. The decrease in material or increase was modeled by means of effective stress, with the development of the solid surface fraction. Any reaction such as ASR length and tension caused by it are described in the form of charges. Due to expansion ASR is modeled as an imposed strain, depending on both the material and the temperature and humidity, considering both the aging effect of the gel as in its early stages. The model was solved numerically by the finite element method and finite difference methods. The proposed mathematical model is validated by comparing the simulation results with some published experimental data.

The authors of the article [6] proposed a mathematical model for the expansion due to alkali-silica reaction. The model is developed based on a single cell having a particular glass particle in spherical shape. A diffusion process water is considered and control the chemical reaction on the surface of the sphere. The gel formed is accommodated in the porous region around the particle. This study determined the optimal size of the glass particle, based on the ability of the porous region has to absorb the products that originate from the reaction. The process is controlled only by the relative humidity inside the pores.

A work in the same direction was developed by [7]. In this work was created a model to determine the pessimum size of the aggregate and also pessimum expansion of concrete. To this end, the model has two steps. The first is considered a diffusion model that is described by Fick’s law, and for the alkali hydroxide ions in solution porous concrete. The formed gel permeates the porous matrix according to the law of Darcy. In the second stage the concrete is considered to be a two-phase composite, where the expansion is determined
by the increase in pressure caused by expansion of the gel in aggregates of different sizes.

In the work [8] researchers present a three-dimensional mesoscopic model that describes the damage caused by ASR in concrete. In the model is generated mortar-aggregate structure based on a three-dimensional finite element mesh. The two phases of mesoscopic model are composed of particles of aggregate and cement paste, which aggregate is considered as purely linear elastic and the cement paste behaves as a damage-elastic material. The aggregate of randomly distributed particles have a volume increase in gel formation. This model reproduces the alkali-silica reaction and the progressive degradation of the material with some precision [9].

The model developed in [10] creates a microstructure based on finite element to analyze the mechanics of a structure subject to RAS. The finite element model includes the microstructure of the aggregate, voids, cement paste, gel and cracks obtained by image analysis. The results for the expansion due to the gel has a good correlation with experimental data.

This work presents the proposal of a model to represent the formation and diffusion of the gel formed by alkali-silica reaction in concrete. First it is create a model using the kinetics of chemical reactions. This initial model consists of the equations obtained by alkali-silica reaction, which is considered as a reaction of pseudo-first order, in this case depending on the amount of silica available. These equations allow to obtain the amount of gel formed over time. The second phase is the diffusion model for the gel of the porous region in the next to the aggregate. The diffusion model takes into account the formed gel concentration over time obtained in the first stage. As a result one obtains a map of the distribution of gel in a representative volume element of concrete. In sequence, we propose a model for the chemical damage due to RAS, using results found in the work [5]. The proposed model is described in the next section.

2 Proposed Model

This model was created in three steps. In the first phase it is created a function to determine the amount of gel formed with the breaking of siloxane bonds. The second layer is a diffusion model, taking into account the amount of gel formed in the first stage. In the third stage, there is obtained a model for the chemical damage due to the ASR in the concrete, using the results of the first two steps.
2.1 Phase I - Gel Formation

Gel formation is based on two main reactions that are described by the equations:

\[
\begin{align*}
\equiv \text{Si} - O - \text{Si} \equiv + R^+ + \text{OH}^- & \rightarrow \equiv \text{Si} - O - R + H - O - \text{Si} \equiv, \\
\equiv \text{Si} - \text{OH} + R^+ + \text{OH}^- & \rightarrow \equiv \text{Si} - O - R + \text{H}_2\text{O}.
\end{align*}
\]

From these equations, it is observed that the gel (\(\equiv \text{Si} - O - R\)) is formed in both stages of the reaction. Thus, using the principles of chemistry kinetics, one can write the following equations:

\[
\begin{align*}
\frac{d[A]}{dt} & = -k_1[A][B]_0[C]_0, \\
\frac{d[X_{sil}]}{dt} & = k_1[A][B]_0[C]_0 - k_2[X_{sil}][B]_0[C]_0, \\
\frac{d[X_{gel}]}{dt} & = k_1[A][B]_0[C]_0 + k_2[X_{sil}][B]_0[C]_0.
\end{align*}
\]

where \([A]\) is the concentration of silica (\(\equiv \text{Si} - O - \text{Si} \equiv\)), \([B]_0\) is the concentration of hydroxyl ions (\(\text{OH}^-\)), \([C]_0\) is the concentration of alkali (sodium or potassium), \([X_{gel}]\) is the concentration of formed gel, \([X_{sil}]\) is the concentration of silanol (\(\equiv \text{Si} - \text{OH}\)) formed, \(k_1\) e \(k_2\) are constant speed.

This model should be considered rates of change for the hydroxyl ions and also to alkalis. However the existence of both is a necessary condition for the reaction to occur. Then, by assumption for this model is considered as the concentrations constant over time, which characterizes this reaction as a pseudo first order reaction in the same manner as is found in the work [11]. Note that this is a proposal to simplify the model, since they work with third-order reactions become excessively complex model.

The equation (3) depicts the rate at which silica is consumed is proportional to the product of the concentrations of hydroxyl ions, alkali and silica present at a time instant \(t\).

In equation (4), it can be observed that the concentration of silanol over time is proportional to its formation in the first step of the chemical reaction (1) and consumption in the second stage (2).

The formation of the gel represented by the equation (5), it was observed that the gel is formed in both stages of the chemical reaction.

As the amount \(B\) (ions hidroxila) and \(C\) (álcalis) were assumed constant over time, one obtains a system of first order differential equations:

\[
\begin{align*}
\frac{d}{dt} \begin{bmatrix} [A] \\ [X_{sil}] \\ [X_{gel}] \end{bmatrix} & = \begin{bmatrix} -\alpha & 0 & 0 \\ \alpha & -\beta & 0 \\ \alpha & \beta & 0 \end{bmatrix} \begin{bmatrix} [A] \\ [X_{sil}] \\ [X_{gel}] \end{bmatrix}.
\end{align*}
\]
where \( \alpha = k_1[B]_0[C]_0 \) and \( \beta = k_2[B]_0[C]_0 \) for simplification. The initial conditions for the problem are: \([A](0) = A_0\), namely, the initial amount of silica available in the beginning of the reaction is given by \( A_0 \). As the reactive aggregate that has an initial amount of silanol-type connector, namely the initial silanol concentration is \([X_{sil}](0) = X_0\). The initial gel concentration is zero, that is, \([X_{gel}](0) = 0\).

Solving the above system using eigenvalues and eigenvectors, is the eigenvalues for the matrix associated with the system: \( \lambda_1 = -\alpha \), \( \lambda_2 = -\beta \) e \( \lambda_3 = 0 \), associated with eigenvectors \( v_1 = [(\beta - \alpha)/\alpha, 1, (\alpha - 2\beta)/\alpha]' \), \( v_2 = [0, -1, 1]' \) e \( v_3 = [0, 0, 1]' \) providing the solution to the system:

\[
[A](t) = A_0e^{-\alpha t} \\
[X_{sil}](t) = \frac{k_1A_0}{k_2 - k_1} (e^{-\alpha t} - e^{-\beta t}) + X_0e^{-\beta t} \\
[X_{gel}](t) = A_0 \left[ 2 + \frac{k_12e^{-\alpha t}k_1e^{-\beta t}}{k_2 - k_1} \right] + X_0(1 - e^{-\beta t})
\]

where \( k_{12} = k_1 - 2k_2 \). Note that this model created was considered only a breach of siloxane bond. The others were not considered, although there also.

The proportionality constants must be determined from data obtained experimentally. In this work the constants were obtained using the experimental results provided at work [12]. The values obtained are: \( k_1 = 0, 1 \) e \( k_2 = 0, 2 \) to an average temperature 38\(^\circ\) C.

![Figure 1: Graphic representation of functions to gel formation and consumption of silica and silanol](image)

In the chart 1 it was observed that the gel concentration is an increasing curve which approximates \( 2A_0 + X_0 \). This is justified by the fact that the use
of ions is proportional to the consumption of silica, i.e., a ratio of 1:1. With the initial concentration of silanol being complete, the final gel concentration is $2A_0 + X_0$.

### 2.2 Phase II - Gel Diffusion

The model for the diffusion of the gel in the concrete matrix is made to a mesoscopic level, i.e., the diffusion process will be considered in the coarse aggregate and the next transition region to the aggregate. Will be considered two different models, since the unit can be located in a region that is in the pores containing water and another one where the pores are subject only to a humidity gradient.

In the first case, as the amount of water is abundant, it is considered only diffusive gel process in a porous matrix containing liquid inside their pores.

Whereas an environment where there is a binary mixture of the two species (gel) and B (water-containing porous matrix within the pores) in which the approach of a stationary medium is applied, that is, the mass transfer occurs only by diffusion where advection is considered negligible, we obtain the equation

$$\nabla (D_{AB} \nabla \rho_A) + \dot{n}_A = \frac{\partial \rho_A}{\partial t}$$

where $D_{AB}$ is binary mass diffusivity in $m^2/s$, $\rho_A$ is the specific mass of species A (gel) in $kg/m^3$, $\rho$ is the density, $kg/m^3$, $\dot{n}_A$ is the mass rate of the increase of species per unit volume due to chemical reactions in $kg/(s \cdot m^3)$.

The above equation can be solved to provide the distribution of concentrations of species $A$.

In this model, species A gel is formed by chemical reaction. As the means whereby the gel is porous spreads, can alter the diffusion equation above for

$$\nabla \left( D_{AB} \frac{\epsilon_p}{\tau} \nabla \rho_A \right) + \dot{n}_A = \frac{\partial \rho_A}{\partial t}$$

onde

$\epsilon_p$ is the porosity of the particle - dimensionless;
$\tau$ is the tortuosity - dimensionless;

The mass rate of increase in species $A$, $\dot{n}_A$ this case will be given by the amount of gel produced in the first step of the model, namely:

$$n_A = [X_{gel}]$$

The chemical reaction occurs when there is high humidity around the unit (assuming that the aggregate is reactive and there alkali ions available). As previously mentioned, the reaction occurs when moisture levels are above 80%. Thus, it is considered that moisture is sufficient to result in reaction.
The aggregate of form in both cases will be considered as elliptical and obtained from a grading curve at work [13].

To resolve these models numerically the equations are discretized on your domain by the finite difference method.

Final answer as it has been a gel concentration in the mesoscopic region considered. This concentration can be used to stipulate the stress and strain associated with the chemical process.

2.3 Phase III - Chemical Damage Model

With the density given in the modeling of reaction and diffusion, we propose the following damage model, taking into account the following considerations. First, the non-damaged concrete density is given by:

$$\rho = \rho_c,$$  \hspace{1cm} (13)

where $\rho_c$ is the density of the concrete. With the formation and diffusion gel density shall be given as follows:

$$\tilde{\rho} = \rho_A + \rho_c,$$  \hspace{1cm} (14)

being $\rho_A$ the density of the gel formed because of the ASR and $\tilde{\rho}$ the density in the damaged state.

It has been $\rho = \frac{m}{V}$, being $m$ mass and $V$ volume and further $\tilde{\rho} = \frac{m}{V'}$, where $V'$ is the volume in the degraded state. Using these relations, we obtain

$$\frac{\rho}{\rho_A + \rho_c} = \frac{V'}{V},$$ \hspace{1cm} (15)

Thus, the above equation is the ratio of the volume after gel formation and the initial volume. The volumetric variation $\Delta V$ is given by

$$\frac{\Delta V}{V} = 1 - \frac{\rho}{\rho_A + \rho_c},$$ \hspace{1cm} (16)

or,

$$v = \frac{\Delta V}{V} = 1 - \frac{\rho}{\tilde{\rho}}$$ \hspace{1cm} (17)

Using experimental data found in the work [5], can be stipulate the chemical damage in terms of volume variation.

$$D = \begin{cases} 0, & \text{se } v \leq 0.001 \\ 2.021v - 0.195, & \text{se } v > 0.001 \end{cases}$$ \hspace{1cm} (18)

As linear regression was used to obtain this equation, it is noted that the value for the damage exceeds the value 1, that is when 100 % of the material
Application to diffusion equation

is damaged. To fix this problem and not lose the model prediction capability, will change to:

\[
D = \begin{cases} 
0, & \text{if } v \leq 0.001 \\
\tanh(w), & \text{if } v > 0.001 
\end{cases}
\] (19)

where \( w = 2.021v - 0.195 \). With this change obtains the damage of a representative volume element concrete.

3 Results and Discussion

The equation (11) was divided by the method of explicit finite differences to two dimensions according to the following equations:

\[
\frac{\rho_{Ai,j}^{n+1} - \rho_{Ai,j}^n}{\Delta t} = \frac{n_{ai,j}^{n+1} - n_{ai,j}^n}{\Delta t} + D_{AB} \frac{\varepsilon_p}{\tau} \left[ \frac{\rho_{Ai+1,j}^n - 2\rho_{Ai,j}^n + \rho_{Ai-1,j}^n}{(\Delta x)^2} \right] + D_{AB} \frac{\varepsilon_p}{\tau} \left[ \frac{\rho_{Ai,j+1}^n - 2\rho_{Ai,j}^n + \rho_{Ai,j-1}^n}{(\Delta y)^2} \right]
\] (20)

where,

\[
\frac{\partial \rho_A}{\partial t} \approx \frac{\rho_{Ai,j}^{n+1} - \rho_{Ai,j}^n}{\Delta t},
\]

\[
\frac{\partial^2 \rho_A}{\partial x^2} \approx \frac{\rho_{Ai+1,j}^n - 2\rho_{Ai,j}^n + \rho_{Ai-1,j}^n}{(\Delta x)^2} e
\]

\[
\frac{\partial^2 \rho_A}{\partial y^2} \approx \frac{\rho_{Ai,j+1}^n - 2\rho_{Ai,j}^n + \rho_{Ai,j-1}^n}{(\Delta y)^2}.
\]

Making \( s_x = \frac{D_{AB}\varepsilon_p\Delta t}{\tau(\Delta x)^2} \) \( s_y = \frac{D_{AB}\varepsilon_p\Delta t}{\tau(\Delta y)^2} \), it has been

\[
\rho_{Ai,j}^{n+1} = s_x [\rho_{Ai+1,j}^n - 2\rho_{Ai,j}^n + \rho_{Ai-1,j}^n] + s_y [\rho_{Ai,j+1}^n - 2\rho_{Ai,j}^n + \rho_{Ai,j-1}^n] + \rho_{Ai,j}^n + n_{ai,j}^{n+1} - n_{ai,j}^n
\] (21)

Solving equation (21) numerically for a time of 10 years, one obtains the distribution density gel in VSR.

The results for density were obtained for the diffusion of the gel formed in only surface of the aggregate, assuming the curve was adjusted for the volume change achieved in [12] with constant temperature of 38 degrees Celsius.
The diffusion constant in the gel were $D_{AB} = 10^{-10}$ m$^2$/s in mortar and $D_{AB} = 10^{-12}$ m$^2$/s in the aggregate, since no experimental results for such diffusion. The gel diffusion coefficient in the aggregate is less than the diffusion coefficient in the mortar, once the porosity is greater in the region of transition aggregate / cement (it is considered that there is added to the gel diffusion).
Figure 4: RVE with elliptical aggregates 50 % area map and chemical damage after 10 years

The charts 2, 3 e 4, can be observed in the chemical damage caused by the RVE RAS. It is observed that the damage is greater in regions containing several smaller aggregates, because there is a greater reduction gel due to greater surface area of the aggregate. The darker regions are aggregated.

4 Conclusion

This paper presents a model for training, dissemination and chemical damage due to gel formation by ASR in a representative element of concrete volume. This model takes into account quantity and silica silanol, and the amount of sodium, potassium and hydroxyl. Moisture is kept constant and temperature effects may be included in Phase I of the model.

As a result it can be seen that when the amount of aggregates is large and a region all variables the RAS, the amount of gel is larger and occurs more damage to the concrete RVE. Regions with few aggregates and within the aggregate suffer little damage because the aggregate is less porous and the gel reaches more easily the transition region of the concrete.

You can justify the results obtained in this study using the following references: [5,6,12]. The work [12] serves to support the gel production over time, which is done in the first phase. Have the stage where the damage is stipulated from the gel concentrations obtained via diffusion equation is justified using the experimental result published in [5]. The work [6] back as a result that the smaller particle diameter causes the accumulation of gel in the transi-
tion region is larger than in smaller particles, which can be seen in these results.

References


Received: March 31, 2015; Published: May 29, 2015