Diffusion–reaction model for the internal sulfate attack in concrete

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HIGHLIGHTS

- A diffusion–reaction model is developed for the internal sulfate attack (ISA).
- The ISA is caused by the oxidation of the pyrrhotite into the aggregates.
- The model can predict the distribution and evolution of the volumetric deformations.
- The proposed model was applied in two real dams.

ARTICLE INFO

ABSTRACT

In the analysis of the behavior of concrete structures affected by expansive problems, it is often necessary to use kinetics models of the reactions involved to assess and predict the magnitude, distribution, and evolution over the time of expansion. In this study, a diffusion–reaction model is developed for the internal sulfate attack (ISA) problem due to the oxidation of the pyrrhotite into the aggregates. The model takes into account the kinetics of the pyrrhotite oxidation under the two main oxidizers and the oxygen transport in the concrete. The dependence of the water content of the concrete is included in the analysis, which affects the reaction kinetics and oxygen diffusion. The developed model is applied to two real dams affected by the ISA. The results obtained validate the model and demonstrate its potential for evaluating and predicting the behavior of structures affected by the ISA.

1. Introduction

Degradation of concrete due to the presence of iron sulfides (such as pyrite and pyrrhotite) in the aggregates is being widely studied in recent years. These sulfides, in the presence of water and oxygen, are oxidized releasing compounds, which can cause a sulfate attack in concrete, called internal sulfate attack (ISA) [1–8].

The sulfate attack is caused by the reaction of sulfate ions with the cement hydration products. The attack mechanism involves several chemical reactions that may produce secondary products such as ettringite, gypsum, and thaumasite [9–13]. An expansion is the result of the formation of these products, which can cause cracking that, in extreme cases, may lead to the disintegration of the mortar or the concrete [14–16].

This type of concrete expansion has been detected in the dam of Rio Descoberto (Brazil) [17] and some Spanish dams such as Graus, Tavàscan, Torán, Rumedo, and Paso Nuevo. The structural implications of the ISA depend of the structure type, characteristics of the cement and aggregates used, as well the environmental conditions.

For a proper evaluation of the impact of such a degradation on the structure, it is necessary to determine the distribution of the expansions inside the structures and the deformations evolution over time. This is usually a difficult task, and the deformations are commonly estimated using phenomenological criteria based on approximations and simplifying assumptions.

Considerable efforts have been made in the development of kinetic models of expansive processes in recent years, especially applied to other types of expansion, more studied in the literature, as the alkali aggregate reaction (AAR) [18,19] and the external sulfate attack (ESA) [20–25]. These models are based on physical and chemical processes, such as transport of reactants and the kinetic of the chemical reactions. This approach allows a direct and consistent determination of the evolution in time, distribution, and generated deformations. This information is very important for the

study and prediction of future behavior of the affected structures, and to support decisions regarding actions against the problem.

The main objective of this study is to propose a kinetic model to predict the evolution in time and distribution of the ISA in the concrete, considering the two oxidants of the pyrrhotite as well as the effect of the environmental conditions. To do this, a reaction–diffusion model is developed, which takes into account the oxygen transport into the concrete and its consumption on the oxidation reactions. The results of the application of this model are compared with data in the literature and are validated with the measured displacements in two real dams affected by the ISA.

2. Background of the diffusion–reaction models

In general, the simulation of chemical reactions requires the consideration of the transport processes involved. The transport of chemical compounds in porous materials is generally considered as a diffusion process, which can be described by Fick's law [26].

A diffusion–reaction system is obtained by the consideration of the transport process with the chemical reactions. Mathematical models are formulated to address this analysis to determine the variation of the concentration of one or more compounds in time under the influence of two processes: the chemical reactions, which transform the substances locally and the transport (by diffusion) of these substances in space [27].

Diffusion–reaction models have been used to study various physical and chemical processes in concrete, such as carbonation [28,29], expansive phenomena such as ASR [18,19,30] and the ESA [20,21], among others. The solution of these models generally involves a system of partial differential equations that must be solved simultaneously for the chemical analysis and transport problem [31,32].

In the study of the ISA by pyrrhotite oxidation in the aggregates, the oxidation reactions mainly depend on the oxygen transport from the outside to inside of the concrete.
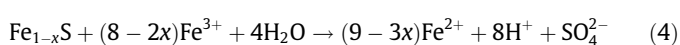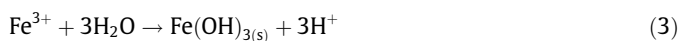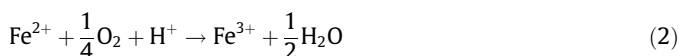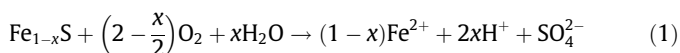
3. Kinetic model for pyrrhotite oxidation in the concrete

For the development of the kinetic model, first, a review of the chemical reactions involved was carried out, and then a diffusion–reaction model of oxygen in the concrete was proposed by taking into account the two main oxidizers of pyrrhotite.
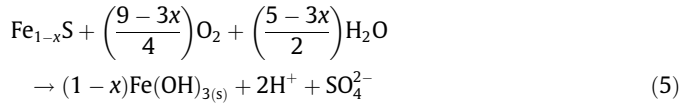
3.1. Pyrrhotite oxidation

The pyrrhotite is oxidized when exposed to oxygen and in the presence of water, leading to the formation of sulfates and iron hydroxides, and causing a decrease in the alkalinity of the system [33]. Oxidation of these sulfides can be initiated by the atmospheric oxygen or iron ions [34].

The following four chemical reactions govern the oxidation process of pyrrhotite by the two oxidation modes mentioned earlier (with x ranging between 0 and 0.125):

$$Fe_{1-x}S + \left(2 - \frac{x}{2}\right)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + 2xH^+ + SO_4^{2-} \tag{1}$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \tag{3}$$

$$Fe_{1-x}S + (8-2x)Fe^{3+} + 4H_2O \rightarrow (9-3x)Fe^{2+} + 8H^+ + SO_4^{2-} \tag{4}$$

In the case of oxygen as the main oxidant, reactions (1) and (2) govern process followed by Eq. (3). This occurs at a pH above 4 [34]. Reaction (1) produces sulfuric acid and Fe^{2+} ions, which are converted into Fe^{3+} ions by reaction (2), and then into iron hydroxide (which is solid) by reaction (3). This process can also be represented by a single overall reaction (5), obtained as a result of the sum of reactions (1)–(3).

$$Fe_{1-x}S + \left(\frac{9-3x}{4}\right)O_2 + \left(\frac{5-3x}{2}\right)H_2O$$
$$\rightarrow (1-x)Fe(OH)_{3(s)} + 2H^+ + SO_4^{2-} \tag{5}$$

In the case of Fe^{3+} ion as the main oxidant, reactions (2) and (4) govern the process. This occurs at a pH lower than 4 [35]. These two reactions occur maintaining a cycle. While reaction (4) consumes Fe^{3+} and produces a greater extent of Fe^{2+}, reaction (2) consumes Fe^{2+} and produces Fe^{3+}, which continues oxidizing the pyrrhotite by reaction (4). This process requires an initial amount of Fe^{3+} or Fe^{2+} to start, in addition to the oxygen in reaction (2).

Both the oxidation processes consume oxygen (Expressions (1) and (2)) and either of them can occur depending on the pH. In this regard, it is well known that the cement paste present in the concrete tends to have highly alkaline pH, although the pH that will define the main oxidizer will not be the pH of the cement paste, but the pH of the aqueous solution in the zone in which oxidation occurs, which, for the case studied, is the aggregate. The oxidation process produces tends to reduce the pH. As a result, an alkaline zone can be converted into acid zone, changing the main oxidizer.

3.2. Diffusion–reactions equations and reaction kinetics

Expression (6) is obtained by applying Fick's Law. This equation allows taking into account the process of transport of oxygen from an external source (the atmospheric air) and its consumption by the chemical reactions inside the concrete.

$$\frac{\partial[O_2]}{\partial t} = \nabla^2(D[O_2]) - \frac{\partial[O_2]_{ri}}{\partial t} \tag{6}$$

where D (m²/s) is the diffusion coefficient of the oxygen in the concrete, $[i]$ denotes the concentration of compound i, and $\frac{\partial[O_2]_{ri}}{\partial t}$ is the consumption of the oxygen by the reaction i.

The kinetics of a chemical reaction can be expressed using a law where the reaction rate is obtained as a function of the concentration of reactants and a kinetic coefficient (k) characteristic of each reaction [36]. For example in a generic reaction A + B → C the rate equation can be written as: $\partial[A]/\partial t = -k[A]^n[B]^m$, where n and m are the partial orders of the reaction (determined empirically). Based on the few available experimental data, the parameters k, n and m cannot be suitably determined for all involved reactions. For these reason first-order kinetics laws (with $n = m = 1$) were adopted, remaining only the parameter k to determine for each reaction.

3.2.1. Oxygen as main oxidant

Reactions (1)–(3) occur when the pH in the zone in which the oxidation occurs is greater than 4. For this case, reaction (5) can be used to describe the overall kinetics. This allows obtaining expressions (7) and (8).

$$\frac{\partial[O_2]}{\partial t} = \nabla^2(D[O_2]) - qk_5[O_2][Fe_{1-x}S] \tag{7}$$

$$\frac{\partial[Fe_{1-x}S]_{r5}}{\partial t} = -k_5[O_2][Fe_{1-x}S] \tag{8}$$