Simulation of Expansion in Cement Based Materials Subjected to External Sulfate Attack

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Abstract
Sulfate attack in concrete structures is considered to be among the major durability concerns in civil infrastructure systems. Proper modeling techniques can help us understand the influence of aggressive environments on the concrete performance more readily and accurately. Such an understanding improves the decision making process in every stage of construction and maintenance and will help in better administration of resources. Aspects of cement chemistry, concrete physics, and mechanics are applied to develop a model for predicting sulfate penetration, reaction, damage evolution, and expansion, leading to degradation of cement-based materials exposed to a sulfate solution. The model is refined to address the interaction effects of various parameters using calibration data available from experiments conducted at the National Institutes of Standards and Technology (NIST). Parameters of the model were refined through parametric analysis, consideration of specific boundary conditions, and calibration with experimental data.

Introduction
Portland cement-based materials subjected to attack from sulfates may suffer from two types of damage: loss of strength of the matrix due to degradation of calcium-silicate-hydrate (C-S-H), and volumetric expansion due to formation of gypsum or ettringite that leads to cracking. Loss of strength has been linked to decalcification of the cement paste hydrates upon sulfate ingress, especially C-S-H, while cracking and expansion is attributed to formation of expansive compounds. Efforts of modeling the durability due to external sulfate attack have received attention only in the past decade [1]. An empirical relationship between ettringite formation and expansion is the basis for many models where the expansive strain is linearly related to the concentration of ettringite [2]. This approach has been incorporated in the 4SIGHT program which predicts the durability of concrete structures [3], as well as in a model that calculates the service life of structures subjected to the ingress of sulfates by sorption [4] or mechanical and transport properties [5].

The general conservation-type equations involve diffusion, convection, chemical reaction and sorption, as the governing phenomena for the transfer of mass through concrete. In the case of sulfates, some authors [6] assume that the process is controlled by reaction rather than diffusion, based on an empirical linear equation that links the depth of deterioration at a given time to the tri-calcium silicate (C_3A) content and the concentration of magnesium and sulfate in the original solutions. A solution of the diffusion equation with a term for first order chemical reaction has been proposed to determine the sulfate concentration as a function of time and space [7, 8]. Similar

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to the recent work by the NIST group, the diffusion coefficient is represented as a function of the capillary porosity and varies with time since capillary pores fill up with the recently formed minerals [4]. Using micromechanics theory and the diffusion-reaction equation, a model that predicts the expansion of mortar bars [9] has been developed for the 1-D case.

A chemo-mechanical mathematical model has recently been developed to simulate the response of concrete exposed to external sulfate solutions [10,11]. The model is based on the diffusion-reaction moving boundary approach and several mechanisms for the reaction of calcium aluminates with sulfates to form expansive ettringite are considered. A schematic model of the present approach is shown in Figure 1. There are three major input parameters categorized under the main categories of 1) Material Parameters, 2) Exposure & Environmental Loading, and 3) Size & Shape of members. The input parameters are used to estimate physical parameters such as the diffusivity, strength, concentration of available calcium aluminates, and the volumetric proportions due to chemical reactions.

The three distinct but coupled problems of sulfate diffusion, calcium aluminate depletion, and crack front propagation posed above are treated as a moving boundary problem as shown in Figure 2. As the time parameter increases, the sulfates diffuse, and then react with aluminates, resulting in hydration products which expand and potentially cause cracking. The cracking causes the coefficient of diffusivity to change from an uncracked material D_2 to a cracked material D_1. This change may be linked to a scalar damage parameter that also affects the material stiffness, E. This damage parameter, ω, is defined from the available models for uniaxial stress-strain response [10].

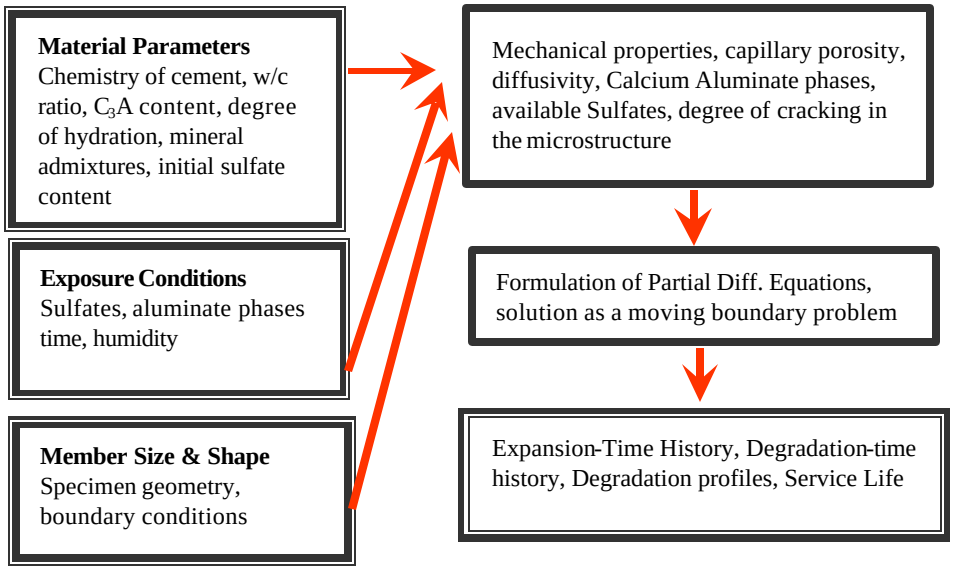

Figure 1. The schematics of the present model for the sulfate attack problem.

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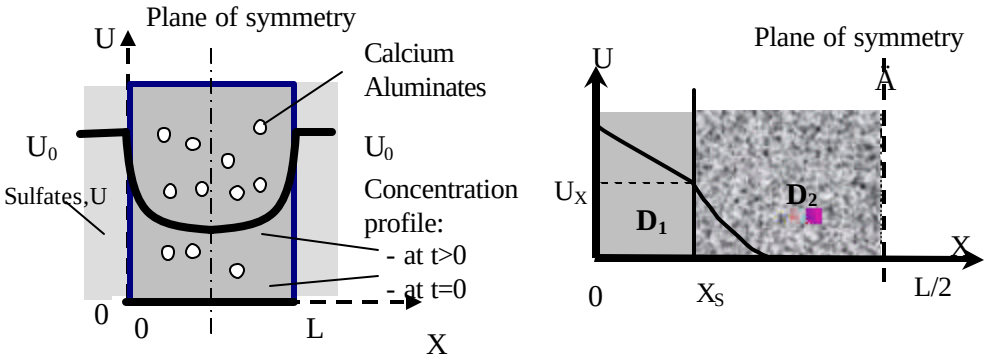

Figure 2. a) Sulfate concentration profile in a specimen of length L subjected to sulfates from at times t=0 and t>0. b) the variation of concrete diffusivity as a function of crack front located at X=X_s

It is assumed that the calcium aluminates may be a blend of three different phases of tricalcium aluminate, tetracalcium alumino hydrate, and monosulfate with parameter γ_i representing the proportion of each phase. The cement chemistry notation is used with (C=CaO, S=SiO_2, A=Al_2O_3 , H=H_2O, and $\bar{S}$ =SO_3). The total calcium aluminate phase is then introduced as: "C_a" (C_a= $\gamma_1 C_4AH_{13} + \gamma_2 C_4A\bar{S}H_{12} + \gamma_3 C\bar{S}H_2$). Each of these compounds may react with the ingressing sulfates (represented in the form of gypsum) according to stoichiometric amounts defined in equations 1-3:

$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \longrightarrow C_6A\bar{S}_3H_{32} + CH \quad (1)$$

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \longrightarrow C_6A\bar{S}_3H_{32} \quad (2)$$

$$C_3A + 3C\bar{S}H_2 + 26H \longrightarrow C_6A\bar{S}_3H_{32} \quad (3)$$

These reactions are lumped in a global sulfate phase-aluminate phase reaction as:

$$C_a + q\bar{S} \longrightarrow C_6A\bar{S}_3H_{32} \quad (4)$$

where $q\bar{S}$ = $(3\gamma_1 + 2\gamma_2 + 3\gamma_3)C\bar{S}H_2$ represents the weighted stoichiometric coefficients of the sulfate phase. For any of the individual reactions described above, the volumetric change due to the difference in specific gravity can be calculated using stoichiometric calculations. The schematic representation of sulfate penetration and reaction is shown in Figure 2 as the exposure time increases. The total calcium aluminate phase is divided into reacted and unreacted amounts and represented respectively as C_{ar} and $C_{au}(x,t)$ according to:

$$C_{ar}(x,t) = C_a - C_{au}(x,t) \quad (5)$$

The coupled differential equations for the depletion of both sulfates and aluminates are solved by means of numerical techniques to take into account the three main effects 1: limited supply of C_3A, cracking induced diffusivity, and the degradation effects of the expansive equations [12]. Figure 3 represents the sulfate and reacted C_3A concentration profiles as a function of exposure time. The effect of time of reaction on the concentration profiles as predicted by Fick's second law with a second order reaction can be observed.

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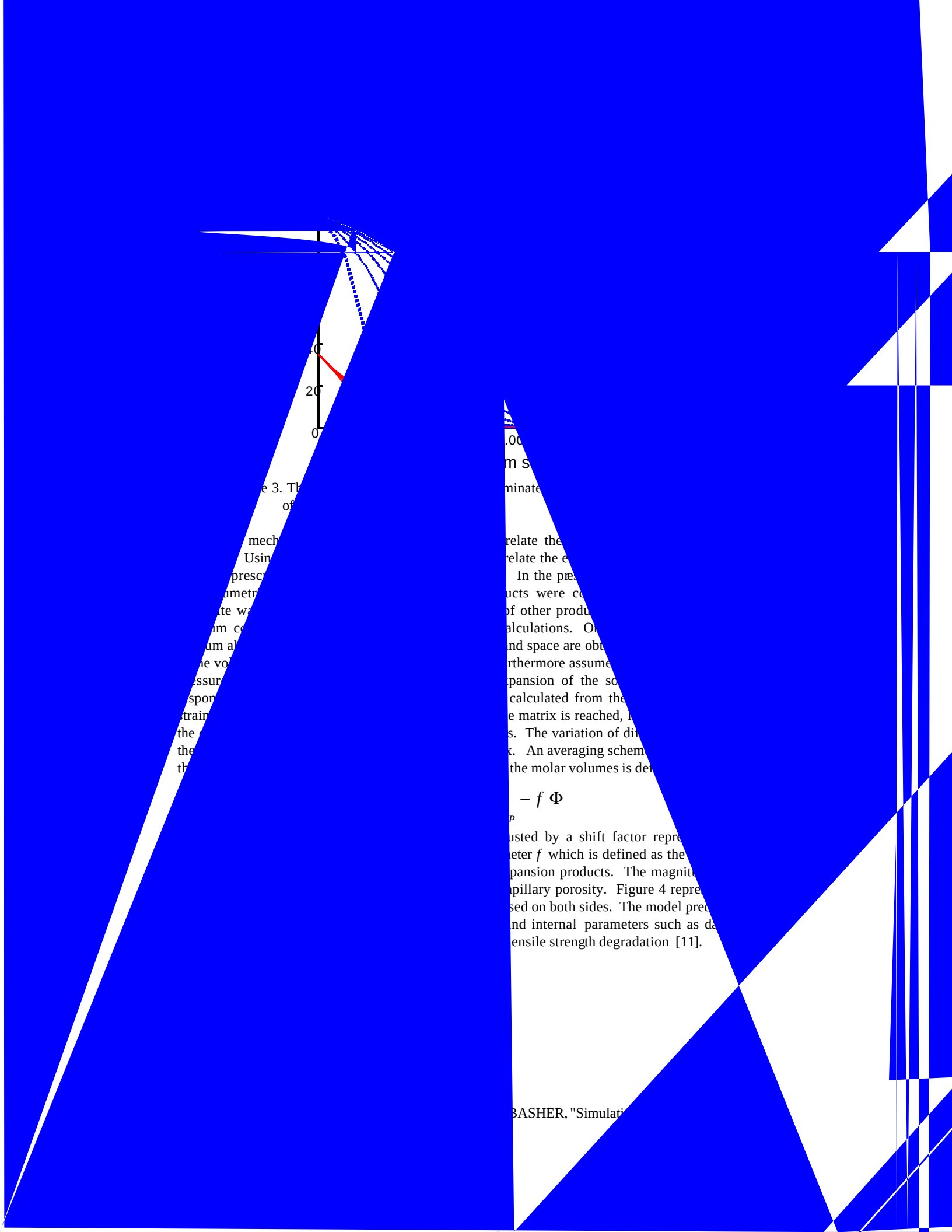

were kept the same, lower values of w/c and the use of pozzolanic materials lead to a lower diffusivity, and hence to a slower reaction, and expansion rate. This mechanism is clearly predicted by the model. When the uncracked diffusivity is reduced by an order of magnitude from $1x10^{-12}$ m^2/s to $1x10^{-12}$ m^2/s the period to achieve the same level of expansion is significantly extended as well. This time factor depends on the level of damage caused by the cracking as well. Note that the higher the level of damage due to cracking as measured by D_1/D_2 ratio, the faster the degradation process. The linear strain measure was used to represent the expansion term here. It was assumed that the linear expansion component would be 1/3 of the volumetric strain under the conditions that the strain is homogeneous and isotropic.

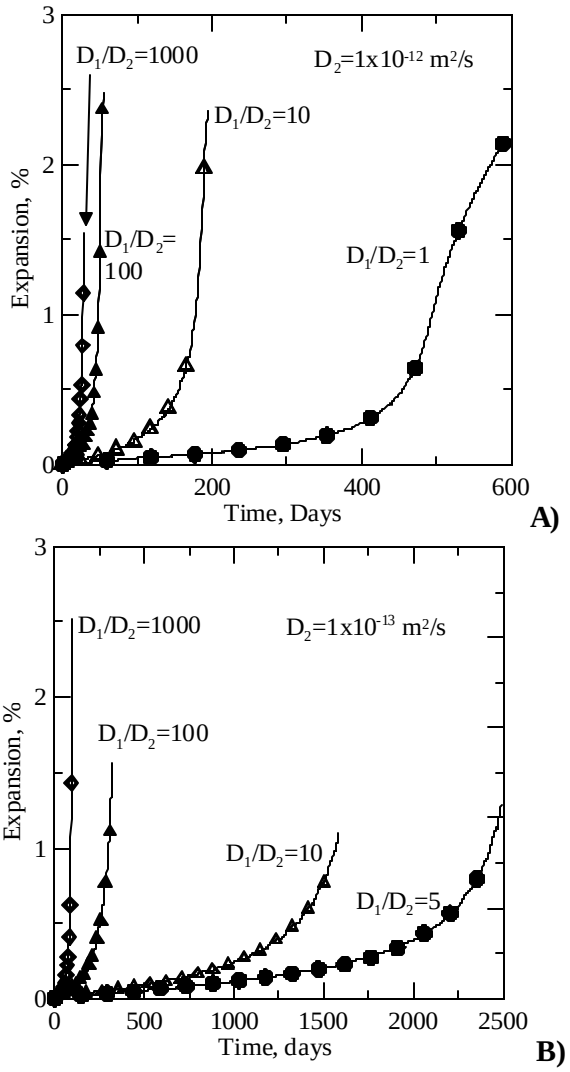

Figure 5 Parametric study of the effect of diffusivity of the cracked material on the expansion-time curves for specimens with various levels of damage due to cracking.

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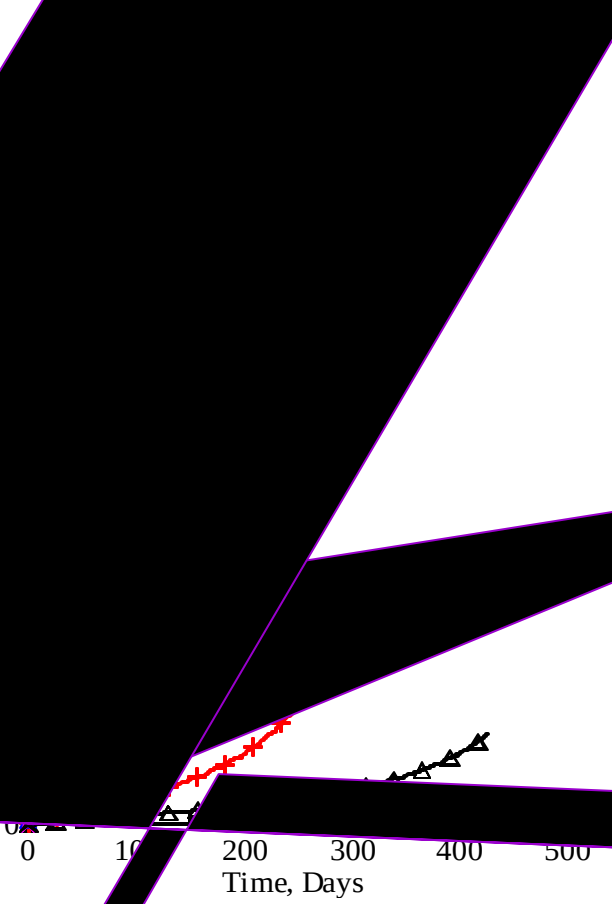

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Effect of initial C_3A content

The resistance of plain and blended concrete (C_3A content between 5% - 12 %) to sulfate solutions has been studied by several authors [14]. Effect of initial C_3A content was studied by evaluating the test results of a series of experiments conducted by Ferraris et al. [15]. A reasonable fit is obtained by adjusting the input data in this case. The results are shown in Figures 8 a, and b. The parameters used in the theoretical calculations are also shown. The values of the parameters for fitting the data are reported as a degree of hydration of 0.9, and an initial sulfate content equivalent to 6 % was assumed. Note that as the initial C_3A increases, the expansion also increases as a function of time. No attempt was made to fit the expansion curve results with the theoretical model and only the trends of the experimental data are simulated using expected values of material parameters. Figure 8b shows a similar set of data obtained for specimens with an initial C_3A at 11.6 %. Note that the rate of expansion in these samples is significantly higher than the previous case, and the simulation graphs are able to address this enhanced expansion activity quite well. Due to the large magnitude of expansive forces expected in this case, the amount of residual stress assumed in this case was set at 10 MPa, as compared to the previous case, which was assumed at 5 MPa.

Conclusions

Applications of a theoretical simulation model to predict the degradation due to external sulfate attack on cement-based materials are discussed. Simulations of the model using a series of parametric studies indicate that the effects of diffusivity of the cracked and uncracked material can play a significant role in the characteristics of sulfate penetration. The amount of initial sulfates in the Portland cement is also an important parameter as predicted by the model. Parameters of the model are chosen to be compatible with the actual mix design of the materials. Effect of initial C_3A content and the age of specimen at time of testing were shown to be predicted favorably by the model parameters.

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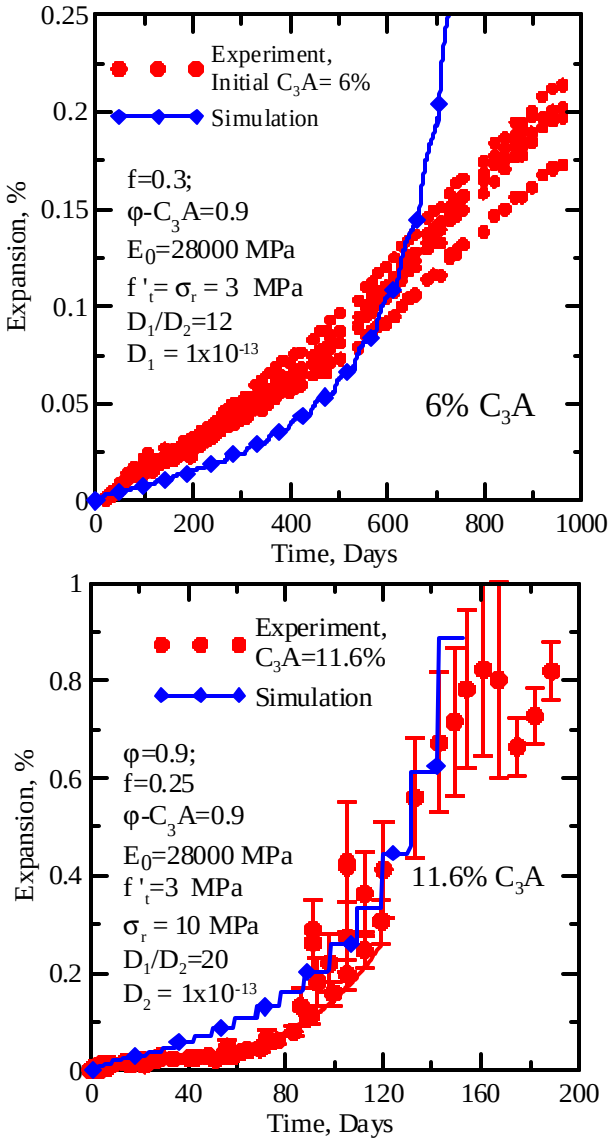

Figure 8 Effect of initial C_3A content on the expansion time response of specimens.

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